HYDROLOGICAL IMPLICATIONS

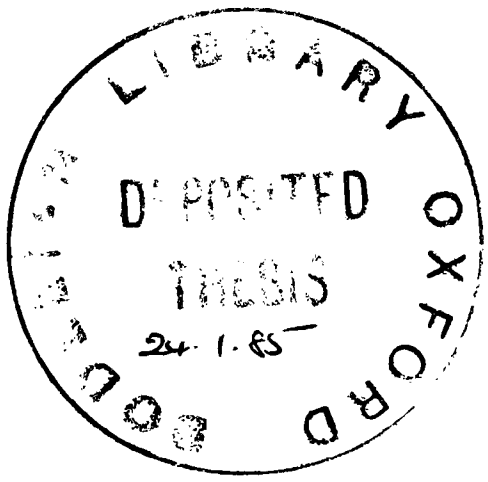
OF

STABLE ISOTOPE DETERMINATIONS

IN U.K. WATERS

(with special reference to the Malham area,

North Yorkshire, and the Lambourn area, Berkshire)



VOLUME 1

by

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Hydrological implications of stable isotope determinations in U.K. waters (with special reference to the Malham area, North Yorkshire and the Lambourn area, Berkshire)

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Abstract

The stable isotopes of oxygen and hydrogen have been employed worldwide as natural hydrological tracers, and most successfully in areas where extremes of climatic seasonality or relief exist. This project aims to assess the viability of the stable isotope technique for studies in the U.K.

Systematic sampling was undertaken over two years in the Malham (Carboniferous limestone) and Lambourn (Chalk) areas. The monthly isotopic input signal in precipitation was found to be clearly definable, but less strongly seasonal than found elsewhere. Larger isotopic variations were revealed in weekly and within-storm samples. Snowmelt appeared to provide the most reliable 'spike' for tracing purposes. An attempt to relate weekly precipitation $\delta^{18}O$ values to air mass characteristics was encouraging for further investigations. Variations of isotope signal with altitude were erratic and not in accordance with normally accepted relationships.

Isotopic variations in groundwaters of both areas, and in surface waters of the Lambourn area, rarely exceeded measurement error, and were close to mean annual values in precipitation. This indicated complete mixing of the input waters over one year or more.

The isotopic range in precipitation was reduced by ~60% in surface waters of the Malham area. Early mixing and storage of water in the soil and/or upper karstic zone were indicated by comparison of the isotope data with conventional hydrological measurements at resurgences, and supported by strong signal attenuation measured in soil moisture. At certain sites, isotopic evidence revealed a persistence of winter recharge into summer baseflow.

A smooth and strongly seasonal isotope signal, discovered in the waters of Malham Tarn, was attributed to evaporation processes and suggests important practical uses.

It is concluded that the general application of the stable isotope technique may be more restricted in the U.K. than elsewhere, but that its provision of a new dimension to conventional data should contribute significantly in the future to selected hydrological studies.

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PART 1 INTRODUCTION

The stable isotopes of oxygen and hydrogen have been successfully employed in many environments, outside the U.K., as natural hydrological tracers. Examples range from applications in the Canadian Rockies (SKLASH et al., 1976) to the Okavango Swamp of Botswana (DINÇER et al., 1979). The most successful applications appear to have been undertaken in climates more seasonally contrasting or else in areas of greater altitudinal relief than are available in the U.K. This situation arises because the strength of the isotope input signal, upon which the tracing depends, is itself dependent upon seasonal variations in temperature and precipitation amounts and, for additional areal distinction, upon altitude; these factors, or isotope 'effects' were first quantified by DANSGAARD (1964).

The use of the stable isotopes for natural tracing, from precipitation through the unsaturated zone to groundwater and to river water, is only one in a suite of possible applications of the environmental isotopes. These range from determinations of palaeoclimates from the isotopic composition of benthic foraminifera (eg. by EMILIANI & SHACKLETON, 1974) to the inference of glacier movement mechanics from isotopic examination of basal ice (eg. by JOUZEL & SOUCHEZ, 1982).

This project was initiated to test the viability, for studies in the U.K., of the stable isotope natural tracing technique. If applicable, the hydrological implications, from comparisons of input and output signals, of stable isotope determinations, could make considerable contributions to conventional understanding of processes in the hydrosphere. The co-operating industrial body in this project (supported by a NERC CASE award) was the Isotope Measurements Laboratory at AERE Harwell which has a particular interest in the prospects for stable isotope hydrology in the U.K. A routine

commercial service of stable isotope measurements is run by the Laboratory, and a knowledge of home market potential is important for the planning of future operations.

Two contrasting areas were chosen for study: the Malham area of Carboniferous limestone in North Yorkshire, and the Lambourn area of Chalk in Berkshire. The detailed reasons for their choice, and area descriptions will be given later, but in brief their hydrologies were well known and they represented opposite extremes in a possible spectrum of flow regimes (after SHUSTER & WHITE, 1971), from predominantly conduit to predominantly diffuse flow. Additional areas, with intermediate flow regimes, had been considered before routine sampling was initiated. These included an area of perched gravel aquifer, named the Three Pigeons Plateau in Oxfordshire (NGR SP 6503), and the catchment of the Sherborne Brook in the Jurassic limestone of the Cotswolds (NGR SP 1415). Unfortunately, both areas proved to be unsuitable because the required background hydrological information was limited in comparison with the areas chosen; for the purposes of this study, concentration on the two extremes of flow type was finally considered to be the most effective. Interest in motorway (M40) runoff affecting the Three Pigeons aquifer and in the development of the Jurassic limestone for water supply might, however, justify the application of the stable isotope technique in these areas in future hydrological investigations.

Monthly monitoring of stable isotopes in precipitation and in ground and surface and intermediate waters formed the basic framework of the study. It was considered important that sampling be performed over at least a two year period at each site, for the definition of responses to a seasonal input signal; this has significant advantages for interpretation over sampling restricted to one seasonal cycle or less. The present study provides an important relatively long period data base for studies in the U.K. It complements and proposes more intensive studies of stable isotope applications in the U.K.

For this study, a total of approximately 1150 stable oxygen isotope ($^{18}O/^{16}O$) analyses, 300 stable hydrogen isotope (D/H) analyses and 140 stable carbon isotope ($^{13}C/^{12}C$) analyses were made by the author in the Isotope Measurements Laboratory. This represents a total of approximately 200 working days of laboratory analyses. Measurements of tritium were provided by the Isotope Measurements Laboratory. All except approximately 50 of the reported chemical measurements were performed by the author; the remainder were carried out by staff of the School of Geography, Oxford.

Part 1 of this thesis introduces the project research design and defines the aims and objectives of this study (section 1.2), after consideration of stable isotope hydrology in the U.K. context. Measurements of stable isotopes are discussed in terms of their relative ratios, in δ notation ($\delta^{18}O$, δD), in units of $^{o}/oo$ or per mil (one tenth of a percent). A necessary background to the nature of the stable isotopes and their application in hydrology is presented in Part 2. This includes explanation of isotope notation and of the isotope 'effects' in precipitation, which are referred to throughout the study.

Of this thesis, the comments on limestone waters (section 1.4), Part 2 and the descriptions of sampling areas and methods in Part 3, each discuss published work. The remainder is original to the author, as are experimental developments in isotope sampling techniques introduced in section 3.5. Results of the study are presented and discussed in Part 4; particular attention is given to the analysis of the stable isotope signal in precipitation since its definition and the understanding of its variations are central to the future use of stable isotope determinations in U.K. hydrology. Finally, included in the conclusions and recommendations for future studies (Part 5) is an assessment of the potential of the stable isotope technique, as indicated by findings in the two study areas.

1.1 Stable isotope hydrology in the U.K. context

In section 2.4.3(a) it will be noted that relatively few hydrological studies using a stable isotope technique have been undertaken in the west coast mid-latitude climatic category, into which grouping falls the U.K. Examples are given, in Part 2, of the diversity of hydrological information which has been obtained elsewhere using this attractive technique. The reasons for the stable isotope technique not being used to their potential in the U.K. in particular may include the following arguments:-

1. The hydrology of the U.K. is well known and additional hydrological techniques are not required.

2. Hydrological investigations in other areas of the world are more critical and therefore use of the environmental isotope technique is more cost effective, for example, in less developed countries.

3. The isotope input signal in precipitation in the U.K. is not sufficiently distinct in seasonality to merit use of the stable isotopes as natural tracers at this timescale.

4. No altitude effect will be available in the U.K. in the input signal for the estimation of mean altitude of recharge, due to the relatively small variations in relief encountered.

5. No distinct modification of the input signal, in terms of evaporation, will be available in the cool, humid climate of the U.K., to enable identification of waters according to their evaporative/non-evaporative source.

In reply to arguments 1 and 2, it may be noted that fundamental problems of aquifer behaviour do remain to be solved. An example is the mode of water movement in chalk in relation to which the contributions of fissure and diffuse/piston flow are still disputed. If a new technique is to be applied, to provide additional data in the study of fundamental hydrological problems, then it is best applied in a situation where much supporting information is available, as in certain aquifers in the U.K. Research by this method may have important implications for the management of water resources in a developed country, for example, in terms of the prevention of nitrate pollution by the identification of the age or sources of the contemporary rise in concentrations in many groundwaters. The technique may therefore be of great economic benefit in a country with a high potable water consumption, relative to total potential potable water supplies, such as the U.K. (where the respective statistics of 17.3 10^6 m^3/day and 20.0 10^6 m^3/day were found in 1975: WATER DATA UNIT, 1977).

Arguments 3, 4 and 5 above, present possible scientific problems in applying the stable isotope technique in the U.K. The theoretical background and reports of empirical studies concerning the seasonality, isotopic depletion with altitude of precipitation and the evaporative modification of the stable isotopes is presented fully in Part 2 of this thesis. Each of these effects occurs naturally in the environment, and strongly influences the distribution through space and through time of the stable isotopes in the hydrosphere. In studies of natural tracing, it is the residual variation of an input signal in the output which provides information of hydrological significance. A relatively weak input signal, however, may still be used in the context of a fast throughput system, as explored for example by MOOK et al. (1974) in the Netherlands. Valentia (Aire) and Lista (Norway) are the nearest stations to the U.K. with records available of stable isotope

concentrations in precipitation from the International Atomic Energy Agency/World Meteorological Organisation (IAEA/WMO) network (reported by YURTSEVER & GAT, 1981). The standard deviations of monthly $\delta^{18}O$ in precipitation at these locations are 1.5 °/oo and 2.3 °/oo and respectively. Even with allowance for local variations in climate regime, it may be expected that $\delta^{18}O$ variations in input in the U.K. will be considerably lower than those, for example, experienced in the more continental Vienna (standard deviation of monthly $\delta^{18}O$, 18.2 °/oo), where natural tracing studies have been successfully carried out (for example, by SAUZAY, 1974).

Preliminary investigations by THORPE et al. (1980) in North Yorkshire, however, revealed that variations in an isotopic input signal may be detected in natural waters in the U.K., in this case waters emerging from horizontally-bedded, karstified limestone. It would appear useful, therefore, to explore further the possibilities of the technique in the U.K., with more complete information concerning the strength of input signal and the degree of attenuation which may be undergone before a signal is lost. This requires not only the use of the technique in a situation where the recovery of the signal is most likely, but also in a critical situation where recovery is less likely, in order to assess the limits of utility of the technique.

With respect to argument 4, above, an absolute maximum altitudinal difference of 1345 m is available in the U.K. (from sea level to the peak of Ben Nevis). This range is exceeded by 8 out of the 14 studies (excluding this study) examined in detail in Part 2. The average rate of $\delta^{18}O$ depletion with height, of the reported studies (excluding this one) is 0.29 °/oo/100 m. Applied to the U.K., this would give a maximum difference of 3.8 °/oo for waters derived from the top of Ben Nevis as opposed to sea level, assuming no mixing of water at lower altitudes. Values of the total altitude effect more typical of the altitudinal ranges found in hydrological basins in the U.K. might be 0.3 °/oo (100 m range) to 2.2 °/oo (800 m range), making the same

assumption of no mixing. Such isotopic differences would be measurable beyond current measurement errors ($\pm$ 0.1 $^{o}/_{oo}$ at 1σ for $\delta^{18}O$) and therefore merit further investigation as to their applicability in the U.K. situation.

Evaporation in the U.K. (argument 5, above) is subdued by the high humidities of an oceanic climate, relative to continental areas at the same latitudes. Mean annual potential evaporation of the order of, for example, 500 mm at Sutton Bonnington in the Midlands, with a range of 5-90 mm on a monthly basis (WARD, 1976) may, however, be sufficient to provide an isotopic modification of waters in certain situations. Empirical examination of this effect is required before it may be dismissed.

The aims and objectives of this study, arising from the contentions discussed above, are stated in the next section. The spatial scale of study and combination of environmental isotopes to be used will be considered in section 1.3; these factors are set in the context of trends in stable isotope hydrology which are examined in detail in Part 2. Limestone waters appeared attractive for this particular study because of the range of flow regimes which they offered. A number of comments will therefore be made relevant to research design in the study of limestone waters, in the form of a brief literature review (section 1.4), which will outline specific areas to which stable isotope studies may contribute.

1.2 The aim and objectives of this study

The overall aim of this study is to test the viability of stable isotopes as natural tracers in hydrology in the U.K. In order to achieve this aim, six objectives are proposed:-

1. To monitor the isotopic input and output signals of contrasting hydrological basins, on a monthly basis.

2. To assess the isotopic altitude effect in precipitation.

3. To determine the attenuation of the signal, from input to output, in the hydrological basins under consideration, and assess its hydrological implications.

4. To assess isotopic variations at intermediate stages between input and output, for the better explanation of signal attenuation, and the assessment of potential for future studies at this scale.

5. To assess the shorter period variations over time with respect to both isotopic input and output for the determination of the error bar in 'seasonal' sampling, and the assessment of potential for future studies, at this finer scale of resolution in the U.K.

6. To assess the utility of the stable isotope technique with respect to conventional hydrological techniques, in the U.K. situation.

A basic framework of monthly sampling is chosen for comparability with other studies which have made use of the seasonal input signal. This choice of timescale is important since few other tracers offer information at this particular periodicity. The translation of these research objectives into a sampling programme in two specific areas is presented in Part 3.

1.3 The scale and combination of environmental isotopes to be used in this study

An intermediate, 'basin' scale is most appropriate for an exploratory investigation into the use of stable isotopes as natural tracers in hydrology.

Study areas are required where hydrological information, obtained using conventional techniques, is already available, to verify results using the new technique and to explore what extra information may be drawn therefrom.

The environmental isotopes of tritium and carbon-13 will be used in addition to the stable isotopes of oxygen and hydrogen. Tritium (^{3}H), the radioactively decaying isotope of hydrogen, will provide information concerning water movement at a greater than 1 year timescale. Carbon-13 ($^{13}C/^{12}C$ or $\delta^{13}C$) will provide information concerning solution dynamics and carbonate species in the water. Further details of these isotopes are given in Part 3.

The choice of a suite of isotopic indicators is in accordance with recommendations made by IAEA (1976), where preference was declared for combined isotopic studies, rather than for concentration on individual isotopic species. Conventional hydrological and geochemical information is to be included in this investigation, since the data are likely to be mutually supporting and any evaluation of a new technique must take place in consideration of information available by more traditional (and possibly more convenient) methods.

1.4 Limestone waters as the subjects of study: some comments relevant to research design

Limestone aquifers were considered suitable for investigation in this study; a range of hydrological responses may be recognised, according to the mechanisms of water transport within a limestone aquifer, and it is suggested that these might provide a range of stable isotope input-output response characteristics.

A complete spectrum of flow types in limestone aquifers may be envisaged, from diffuse, Darcian-type flow, to confined flow in pipes or conduits. Figure 1.1 illustrates such end-members, together with two possible

intermediate situations which incorporate the ideas of recent developments in limestone hydrology, viz. fissure flow in porous limestones such as Chalk, and the presence of a highly-fissured subcutaneous zone in massive limestones, such as the Carboniferous limestone. The development of different flow regimes in different limestone types is due to, and reflected by, the range of primary and secondary porosity in relation to pore size in the host limestone rock. This point is illustrated in fig. 1.2. Massive limestones show the importance of secondary voids in contributing to total rock permeability, whereas higher primary porosity is found in chalks.

In choosing to study the stable isotope hydrology of limestone aquifers in the U.K., a convenient contrast is available, within one aquifer type, and also within a particular field study area, where a more narrow range of conduit and diffuse flow may be found. Additionally, particular aspects of the hydrology of these aquifers, which have previously been explored using conventional hydrological techniques, may benefit from examination using the stable isotope technique. Such aspects include:-

(1) The indexing of flow regime in limestone aquifers.

(2) The role of the subcutaneous zone in karst hydrology.

(3) The rapid transmission of precipitation to groundwater or streamflow, in chalk terrains.

These aspects will be examined in turn, in order to place the stable isotope method in the context of conventional hydrological research in limestone aquifers, and also to indicate how a research design of an exploratory nature may be adopted to contribute to the analysis of particular hypotheses.

1.4.1 The indexing of flow regime in limestone aquifers

The use of a single index or combination of indices to describe, and to enable direct comparisons of aquifer behaviour, is an attractive objective in hydrological research. Several indicators have been proposed for limestone aquifers. SHUSTER & WHITE (1971) calibrated measures of chemical and discharge variability of karstic springs in the Nittany Valley, U.S.A., against the classifications of 'diffuse' and 'conduit' types of flow, the classifications being determined from (qualitative) hydrogeological considerations. The coefficient of variation of total water hardness (CV %) at each of 14 springs was calculated from sampling for chemical analysis every 2-3 weeks, where:

$$CV\ \% = \frac{\text{Standard deviation (water hardness)}}{\text{Mean (water hardness)}} \times 100$$

Water hardness results from the presence of alkaline earth ions in solution, and in particular may be attributed to the dissolution of the carbonates of calcium and magnesium in waters issuing from limestone aquifers. The complex process of limestone dissolution has been investigated in detail by many workers (eg. GARRELS & CHRIST, 1965; THRAILGILL, 1968; PICKNETT et al., 1976; WIGLEY et al., 1978). Where the major dissolving agent is carbonic acid, eg. derived from soil CO_2, the process may be simplified and expressed (for the case of calcium carbonate dissolution) by the equations shown in fig. 1.3. The reactions depicted occur in equilibrium, ie. they may proceed in a forward or reverse direction, and the equilibrium constants between the steps are known. Most of the reactions take place rapidly, but the changes in phase occur relatively slowly (PICKNETT et al., 1976). Limited by these slower steps, the transfer of calcium carbonate into solution, into flowing water, is to a certain extent limited by the parameters of solution dynamics, such as the area of contact between solute and solid, and the opportunity for diffusion through the contact layer, which is dependent upon

small-scale turbulence within the fluid (EWERS, 1978). Thus, with variations in these parameters, variations in water hardness may result.

SHUSTER & WHITE (1971) found the coefficient of variation (CV %), previously defined, to be the best of the 'critical parameters' investigated to distinguish diffuse and conduit type flows (the end- members of the spectrum being shown as (a) and (d) in fig. 1.1). The following classification held:-

Conduit-type springs : 10% < CV % < 24 %

Diffuse-type springs : CV % < 5 %

It is implied that greater variability of concentrations in conduit-dominated systems is due to dilution effects and/or flushing out of the more concentrated solutions normally held in smaller fissures, whereas in diffuse-flow systems, fluctuations in water movement are subdued, and relatively constant solute concentrations result.

This approach of indexing has been welcomed by many workers (eg. EDE, 1971), but may be criticised because:-

(1) the implication of solution dynamics in differentiating the two flow regime types is not adequately reflected in a measure of the concentration variability alone;

and,

(2) the diffuse flow category may include percolating waters which enter solutionally widened fissures close to the surface and flow rapidly to the spring; and exceptionally, diffusely flowing waters may be mis-classified as conduit-type waters using this scheme.

The first criticism has been met by the use of measures of solution equilibria and their variability in karst waters. Reference back to the chemical equilibria in fig. 1.3 shows the carbonate dissolution process to be fundamentally controlled by the partial pressure of CO_2 in solution. The same pCO_2 value may, however, bring about different levels of water hardness because the three phases in the dissolution process (solid-liquid-gas) may not co-exist. If they do, the system is termed 'open', but if the supply of gaseous CO_2 is not available, once the water enters the zone of contact with the solid to be dissolved (ie. the carbonate rock), the system is termed 'closed'. Figure 1.4 illustrates schematically the contrasting open/closed recharge conditions, together with a representation of the possible paths of chemical evolution. The processes are described in detail elsewhere (eg. by SMITH & MEAD, 1962).

As an example of the application of solution equilibria, DRAKE & HARMON (1973) were able to separate out in a linear discriminant function analysis, six groupings of water type in the Central Pennsylvanian region, according to the sample saturation index with respect to calcite (SI_c) and the sample equilibrium partial pressure of carbon dioxide (pCO_2). These groupings are plotted in fig. 1.5 in which, for example, diffuse springs are distinguished from relatively under-saturated stream recharge waters using this method. In addition to the advantages of providing a classification system, this approach was considered useful to define the chemical evolution of water moving through the carbonate drainage system, viz. : (a) in terms of recharge conditions, of 'open' and 'closed' recharge, with respect to the supply of CO_2 with progressive solution, by examination of pCO_2 and SI_c values together, and (b) in terms of the measurement of residence time of water within the system, principally from examination of SI_c values.

The second criticism of SHUSTER & WHITE's schema, made by NEWSON (1972), was exemplifed by ATKINSON (1977). Coefficients of variations of water

hardness at Cheddar, Rodney Stoke and Wookey Hole springs (Mendip, U.K.) indicated diffuse flow, whereas hydrogeological evidence showed 60-80 % of flow to be through conduits. This confusion arose because over 80% of the recharging water, better termed percolating than diffuse water, had initially passed through a substantial soil layer before entering conduits in the limestone. A two-way categorisation of flow characteristic (diffuse/conduit) by source region (authogenic/allogenic ie. within/outside limestone area source), illustrated in fig. 1.6(a), might assist in a more exact description of the particular hydrologies.

It may be noted, however, that the speed of travel of water, from point of recharge to resurgence, is a fundamental description which is missing in the geochemical description of limestone waters. Artificial tracing studies tend to indicate times of travel between discrete points.

PITTY (1976, 1980) attempted to express the residence time of whole water bodies, in terms of temperature lags of resurgence waters behind air temperatures. The variability of monthly resurgence temperatures through time (CROWTHER & PITTY, 1982) was also thought to indicate the depth of circulation of and/or mixing in the limestone aquifer. Both approaches must be viewed with caution. Although providing attractively simple and very convenient indices, their physical basis is less well founded (BERTENSHAW, 1980). The complex process of (bi-directional) heat exchange between rock and water, upon which the second suggestion depends, negates the utility of temperature as a near 'conservative' tracer, which is required in the approach of the first suggestion.

Stable isotopes may be proposed here, as potential indicators of flow paths with respect to the actual water passing through a limestone aquifer. Figure 1.6(b) illustrates how particular combinations of variability in a chemical parameter and the variability of stable isotope content, measured from periodic spot-sampling of a resurgence, over a period of one year or

more, may be interpreted with respect to the aquifer hydrology. Post-recharge flow mechanisms in particular are distinguished, where purely chemical indices might otherwise reflect a loss of information, due to equifinality in the solution process (different paths of chemical solution producing the same end concentration or degree of saturation). It is tentatively hypothesised that stable isotopes may contribute to an improved indexing of flow regime in limestone aquifers. Testing of this hypothesis requires periodic sampling of resurgent waters, from a range of recongisable flow regimes, with both isotopic and chemical analyses undertaken.

1.4.2 The role of subcutaneous flow in karst hydrology

A recent development in karst hydrology has been the increased appreciation of the existence of a highly fissured layer of limestone near the surface, which may form an effective 'perched' aquifer (see fig. 1.7). This was termed the 'zone épikarstique' by French hydrologists of the Laboratoire Souterrain du Centre National de la Recherche Scientifique at Moulis, from work undertaken in the French Pyrenees, eg. by MANGIN (1974), and also by FRIEDRICH (1981) in the Carboniferous limestone aquifer of the Mendip Hills, U.K. Other workers have preferred to call this the 'subcutaneous zone', eg. GUNN (1981) and WILLIAMS (1983).

The importance of this zone lies in its supply of a constant 'baseflow' via cave drips or seepages to the phreatic zone. Water storage in fissures of the phreas was previously thought to be quantitatively the most significant, as shown in fig. 1.8 and discussed, for example, by ATKINSON (1977). Fissures in the upper 5-15 m of the aquifer are now thought, however, to provide the most significant water storage, in certain aquifers, as was illustrated schematically in fig. 1.7 for the Mendip Hills.

Traditionally artifical tracers, applied at discrete (frequently swallet) input points in karst areas, have been used to investigate particular problems of aquifer dynamics, for example using fluorescent dyes (reviewed by SMART & LAIDLAW, 1977) and/or Lycopodium spores (DREW & SMITH, 1969). This emphasis upon discrete inputs may account for the earlier negligence of diffuse flow mechanisms and fissure storage. Natural tracers offer greater potential for examination of the latter processes, due to their widespread input. The category of natural tracers may include innovations such as the use of microflora (FRIEDRICH et al., 1982) as well as stable isotopes.

Examination of stable isotopes in areas of karst have traditionally concentrated upon the altitude of recharge and the sources of isotopically distinct waters (eg. SCHOTTERER et al., 1979 in Switzerland; DINÇER & PAYNE, 1971, in Turkey, respectively). More recently, separation of karst hydrographs has been attempted, by the identification of quickflow and baseflow. Work in particular by BAKALOWICZ et al., (1974) has contributed to this subject area. From sampling of three karstic springs in the French Pyrenees, a damping of the isotopic input signal was recognised. This was attributed to processes occurring in the subcutaneous zone. Mixing, however, appeared to be incomplete, and the varying responses of different parts of the saturated zone in individual events were thought to be the cause of the inhomogeneity.

It may be hypothesised that stable isotopes as natural tracers may contribute to the assessment of subcutaneous processes in a karst aquifer. Testing of this hypothesis requires the sampling for stable isotope analysis of karstic resurgences in different stages of flow and/or sampling over a storm hydrograph, for comparison with known isotopic input signals. Periodic sampling of flow through the unsaturated zone, in conjunction with periodic sampling of resurgence and groundwater may also provide useful information

concerning subcutaneous mixing and storage by making use of the seasonal isotope input signal, should this be an appropriate timescale for examination.

1.4.3 The rapid transmission of precipitation to groundwater or streamflow in chalk terrains

Traditionally, flow in chalk has been considered to be near-Darcian, through a relatively porous, homogenous medium. Resurgent waters from chalk aquifers have typically shown only slight variations in carbonate hardness, and other chemical parameters. Discharge normally follows a seasonal pattern, lagged behind that of the input of effective precipitation (precipitation minus evapotranspiration).

Certain inhomogeneities in the chalk, however, have become evident, first from increased hydrological instrumentation of the saturated zone. MacDONALD & KENYON (1961), for example, report apparent aquifer inhomogeneity from continuous river and well water-level recordings in Southern Britain. Variations in transmissivity in the saturated chalk are now well documented, from pumping test analyses (JONES & RUSHTON, 1981) and have been related to specific topographic positions (INESON, 1962).

Interest has been sustained in the chalk due to its importance as an aquifer for potable water supplies, providing, for example, 15% of all Britain's water supply (FOSTER, 1975). Two particular features of chalk groundwater have prompted research to be extended to the unsaturated zone. These are (a) apparently old ages of groundwater, inferred from their low tritium concentrations, and (b) recent rises in nitrate levels in chalk waters.

SMITH et al. (1970) examined a core of Upper Chalk down to the water table at 27 m from the Lambourn catchment, Berkshire, U.K. Measurement of the natural tritium concentration from interstitial waters in the vertical profile was used to provide information on the downward movement of water in the strata since the production of thermonuclear tritium in 1954, which reached a

peak in 1963-64 (explained in section 3.3.1(b)). This profile is included in fig. 1.9(a). A mean downward seepage velocity of 0.88 m/yr was calculated. Models of water input were examined to explain the observed tritium peak, with some tritium also at depth, presumably due to water penetrating down fissures. The best fit model was found where approximately 85 % of the total downward flow was assumed to be by intergranular seepage (fig. 1.9(b)). HEADWORTH (1972) welcomed this explanation and identified three types of water transmission in the unsaturated zone, after the analysis of chalk groundwater fluctuations, as shown by autographic water level records. These were:-

(1) actual percolation, as identified by the labelled water of SMITH et al. (1970); rate $\sim$1 m/yr;

(2) apparent percolation, rainwater at the top of a chalk profile displacing that at the bottom; rate $\sim$4 m/day;

(3) percolation pressure which propagates through the soil air to produce a rapid water table response to intense rainfall at the surface; rate $\sim$10 m/hr.

FOSTER (1975), however, was unable to accept the model proposed by SMITH, on the grounds that surface runoff was never observed, as might be predicted, after periods of high-intensity rainfall. An alternative model was suggested, in which the self-diffusion of thermonuclear tritium occurred, from flow predominantly through high-angle joints in the unsaturated zone, into the saturated pore space of the rock matrix, shown in fig. 1.9(c).

The debate continued, with measurement of additonal profiles by Smith which appeared to corroborate his model, and with a re-analysis of modelling by FOSTER & SMITH-CARRINGTON (1980) which equally accounted for the observed variations. SMITH's model explains low groundwater levels in chalk by the overall slow recharge mechanism whereas FOSTER's model infers a 'filtering

out' of tritium into interstitial spaces, except in high flow conditions when direct flow down macropores allows for recharge of recent waters to the saturated zone.

Additionally, because of interest in pollution control, the movement of nitrates through the Chalk has been investigated. At the Letcombe Laboratory of the Agricultural Research Council, MERCER & HILL (1977), MERCER et al. (1978) and BURFORD et al. (1979) investigated movement of water and nutrients through cultivated monolith lysimeters, using tritiated water, nitrogen-15 and chlorine-36, introduced in fertilizers. Results have tended to agree best with the FOSTER model, indicating that the present high nitrate levels in natural chalk waters may result from current practices of using inorganic fertilisers (since World War II), rather than from the 'agricultural revolution' which has occurred in the U.K. over a period of several centuries.

In contrast with studies of percolating recharge in the unsaturated zone, evidence of turbulent flow in discrete fissures, over large distances, has been shown by ATKINSON & SMITH (1974) in the Upper Chalk of South Hampshire, and resulted in extreme caution being recommended, for the disposal of wastes. Swallets were found to occur at the surface, and such karstification of chalk is most likely where allogenic water enters from overlying impermeable strata, a phenomenon which may be quite common in Britain (eg. where glacial drift overlies; LLOYD, 1980).

Analysis of chalk water for stable isotopes has taken place in a limited number of hydrological process studies. Periodic (monthly) sampling of the River Eure, issuing from the Normandy chalk in France by CONRAD et al. (1979) showed variations in tritium of 11-112 TU*, compared with a range of 11-186 TU in contemporary monthly rainfall, indicating incomplete homogenisation of waters. Almost complete smoothing of the stable isotope signal occurred, however (mean $\delta^{18}O$, -6.9 $^{o}/_{oo}$). Only slight spatial $\delta^{18}O$ variations (range 0.3 $^{o}/_{oo}$) were found by BLAVOUX & PANETIER (1978) in a

* Tritium units - see section 3.3 1 (b), p. 117.

survey of chalk springs and wells in the Joigny-Toucy region (Yonne, France). Re-sampling through time supported the conclusions that (p.72)

> "les vitesses moyennes d'écoulement sont fiables et que l'aquifère est homogène. L'essentiel du flux à l'exutoire a donc transité par la matrice microporeuse".

From examination of the English chalk, BATH et al. (1982, 1984) have shown the seasonal stable isotope input signal to be lost in the unsaturated zone within 5 m of the surface in Cambridgeshire, and within 7 m in Dorset. Lysimeter drainage and saturated zone groundwater were sampled in Cambridgeshire, and isotopic measurements agreed with interstitial waters at the depths of complete mixing, as shown in fig. 1.10. Downwards displacement of the annual cycle near the surface is in the order of 1 m per year which is consistent with the estimates of tritium movement in the chalk by SMITH et al. (1970). In an examination of the data of BATH et al.(1982), with respect to soil physics, WELLINGS & COOPER (1983) note that high matrix potentials preclude fissure flow in chalk for much of the year, but that high local variability in chalk physical properties and also variations in components of the water balance make an assessment of its occurence problematic, without further research.

If we hypothesise that direct, by-pass fissure flow is volumetrically unimportant relative to other modes of recharge in chalk terrains, the hypothesis may be tested by the sampling of chalk water from the saturated zone. Any variation through time in the stable isotope composition of such waters would tend to falsify the hypothesis, assuming that the piston flow mechanism allows sufficient time for the mixing of waters on a greater than annual basis, and causes the smoothing of isotope signal in the unsaturated zone. Any variation with time of stable isotopes in chalk water would provide evidence that waters are not homogenised at the annual timescale. Periodic sampling of ground and resurgent (surface) waters in a chalk area are therefore required in order to examine this hypothesis.

The choice of study areas and the development of a research design to satisfy the aims and objectives and to explore the hypotheses considered in this introduction are presented in Part 3 of the thesis.

PART 2 BACKGROUND TO THE STABLE ISOTOPES

This part of the thesis gives a full background for any isotope study of natural waters in the U.K. and is included here in fulfilment of clause VI.VIII.5 part (i) of the current University Examination Regulations. It is important to include such background as this is the first doctoral thesis, to the author's knowledge, to be presented in a geography department upon the subject of stable isotope hydrology in the U.K. This part may be read, nevertheless, separately from the rest of the thesis, except for references to isotopic notation, which are essential, in section 2.2.4.

If the reader wishes to pursue the environmental monitoring project, he is recommended to proceed to Part 3.

2.1 Introduction

A background to the stable isotopes is presented below, in terms of their physical nature, detection, expression and natural variations. The fractionation processes which cause isotopic variations (section 2.2.5) are of particular importance in the understanding of applications in the isotopes. A review of the natural isotope variations in the hydrological cycle (section 2.3) includes both theoretical considerations and empirical observations. Trends are identified in the applications of stable isotopes in hydrological studies (section 2.4) which led to the identification of the research subject (section 1.1).

2.2 The nature of the stable isotopes of oxygen and hydrogen

2.2.1 Introduction to the isotopes and their nomenclature

Atoms of a given element having the same number of protons in their nuclei but having different atomic masses are called isotopes (from the Greek,

iso=equal topos=place) because they occupy the same place in the Periodic System (RANKAMA, 1954). The differences in atomic mass between isotopes are due to their having different numbers of neutrons in the nucleus, as shown schematically in fig. 2.1.

The isotopes of hydrogen and oxygen are of prime interest for hydrological studies since they are the constituents of water itself. The most abundant hydrogen isotope, of mass 1, is designated ^{1}H or, more often, simply H, as will be used here. The heavy isotopes of hydrogen with masses 2 and 3 have the individual names of deuterium and tritium respectively. The nomenclature of D and T is commonly used instead of the more correct form of ^{2}H and ^{3}H, and will also be used here, in accordance with most of the isotopic hydrological and geochemical literature. No individual nomenclature exists for the isotopes of oxygen of masses 16 (the most abundant), 17 and 18 ; these are designated ^{16}O, ^{17}O and ^{18}O respectively.

Nuclides are either stable, since no change with time is detectable in them, or unstable because they decay radioactively, at a measurable rate, to form other nuclides. In 1973, 300 stable isotopes had been recognised whilst over 1,200 were known to be unstable (HOEFS, 1973). Tritium, is unstable and exhibits beta decay. The remainder of the isotopes of hydrogen and oxygen specified above are stable.

Variations in the distribution of the stable isotopes in nature occur due to the physical and chemical effects of isotope substitution. These produce fractionation effects which will be considered in terms of δ-notation, following a brief historical background to the discovery and measurement of the isotopes.

2.2.2 Historical background

It was first suggested by the English chemist, SODDY in 1910, that atoms of the same chemical element might exist with different atomic weights, and be distinguishable by their physical properties (SODDY, 1913; ASTON, 1933;

FERRONSKY & POLYAKOV, 1982). Techniques were developed specifically to search for isotopes (GAT, 1981a); GIAUQUE & JOHNSTON (1929) discovered the isotopes of oxygen with mass number 18 (most common mass 16) and later the isotope with mass 17, from data obtained by atmospheric absorption spectrography. A hydrogen isotope with mass 2 was identified using an enriched gas, by UREY et al. (1932) on a mass spectrograph.

Impetus for further studies continued due to the awareness of isotopic variations in standard elements to which specific atomic weights had previously been referred. The distribution of isotopes in natural substances, including water, was investigated. Many early measurements of water were based on density techniques, resulting in rather poor levels of accuracy (FERRONSKY & POLYAKOV, 1982). A more satisfactory method which emerged was the technique of separating the different masses in a beam of ions of the same charge by passing them through a vacuum chamber containing electric and magnetic fields, where they were deflected according to their mass and focused on a photographic plate. This was the origin of modern mass spectrometry, the major advance in which came with the development of the Nier-McKinney mass spectrometer (NIER, 1947; McKINNEY et al., 1950). The principal improvements included in this machine, which enabled small differences in isotope abundances to be measured, were the use of a double gas leak inlet (the "McKinney valve", for close comparison between sample and standard) and a double collector (so that simultaneous measurement of the ratio between one mass beam and another became possible). In addition, better electronic components gave increased stability and all these factors contributed to the achievement of an exceptionally high precision of measurement. The modern mass spectrometer, eg. the VG Isogas 602E used at AERE Harwell, is closely based on the Nier-McKinney development, and the operating principles of this are presented in Appendix A.

Development in preparation techniques for the analysis of hydrogen and

oxygen isotopes in water were made by FRIEDMAN (1953) and EPSTEIN & MAYEDA (1953) respectively. In the light of natural variations accurately identified by mass spectrometry, suggestions for the applications of isotope analyses were made. These important studies initiated systematic research into the natural principles governing the distribution of the stable isotopes of oxygen and hydrogen in the hydrosphere, and their application to the solution of scientific and practical problems.

2.2.3 Natural abundance of the isotopes

The average terrestrial abundances of the isotopes of hydrogen (including tritium), oxygen and also the isotopes of carbon, are summarised in fig. 2.1. Relative abundances are normally expressed in preference to absolute abundances since the former may be more accurately measured for stable isotopes using a double-collecting mass spectrometer. Also, as will be discussed in section 2.2.4, relative abundances are usually given as per mil ($^{o}/_{oo}$) differences ($^{o}/_{oo}$ being one tenth of a percent) between the sample ratio and a chosen standard.

The two stable isotopes of hydrogen and three of oxygen may combine in nine ways to form possible water species. Of these, the average relative abundances of the four most common species, $H_2{}^{16}O$: $H_2{}^{18}O$: $H_2{}^{17}O$: HDO are given by 10^6 : 2000 : 420 : 320. In terrestrial materials, the ^{17}O geochemistry echoes that of the 5.5 times more abundant ^{18}O, and is not normally considered separately (GAT, 1981b; FRITZ & FONTES, 1980).

FERRONSKY & POLYAKOV (1982) found the maximum range of variation in the ratios D/H and $^{18}O/^{16}O$ in natural waters to be 70% and 9% respectively, of the average isotopic abundances. Precipitation over the polar regions was found to be the most depleted (relatively deficient in heavy isotopes) and water of enclosed basins in arid areas to be the most enriched (relatively plentiful in heavy isotopes). Such variations are over 300 times the current measurement error for natural waters using a mass spectrometer.

The absolute limits of isotope variation are considerably greater when atmospheric molecular hydrogen, oxygen and carbon dioxide are considered, together with inclusions of the isotopes in the composition of mineral and organically bound materials. Thus MAGARITZ & GAT (1981) summarise the observed variability in oxygen and hydrogen isotope abundance of natural materials as falling in the ranges -50 to +50 $^{o}/_{oo}$ for $^{18}O/^{16}O$ and -500 to +300 $^{o}/_{oo}$ for D/H, when measurements are expressed with respect to a Standard Mean Oceanic Water, or SMOW (see section 2.2.4 for discussion of this reference water). The distributions of oxygen-18 and deuterium in natural materials are presented schematically in figs. 2.2 and 2.3, respectively.

These distributions are largely the result of processes of isotope fractionation within a closed system, with only minor gains and losses of the isotopes in terrestrial material (MAGARITZ & GAT, 1981).

2.2.4 The expression of stable isotope measurements

2.2.4(a) δ-notation

It has already been indicated that the measurement of absolute isotope abundances is not normally attempted, but that a double-collecting mass spectrometer allows high accuracy determinations to be achieved of relative abundances. The isotopic variations observed in natural substances are normally expressed as the relative difference in the isotopic ratio of a sample, with respect to a specified reference. This difference is designated by the greek letter δ (delta) and is given by:

$$\delta_{\text{sample-reference}} = \frac{R_{\text{sample}} - R_{\text{reference}}}{R_{\text{reference}}} \times 1000 \ (^{o}/_{oo}) \qquad (2.1)$$

where $R = {}^{18}O/{}^{16}O$ or D/H concentration ratios, in the case of water. Note that R is always written as the ratio of the heavy (rare) isotope to the light (common) isotope. As differences are usually small, it is convenient to express these in units of per mil (parts per thousand or $^{o}/_{oo}$). Positive δ

values show the samples to be enriched in the heavy isotope species with respect to the reference, negative values indicate samples depleted in the heavy isotope species. For example, a sample with $\delta^{18}O$ value of +10.0 ($^{o}/_{oo}$) is enriched in ^{18}O (or has a greater $^{18}O/^{16}O$ ratio) by 1 per cent, relative to the standard. FRIEDMAN & O'NEIL (1977) state, in justification of the δ-scale, that a knowledge of the relative isotope variations provides sufficient definition for both geochemical and hydrological investigations. Absolute isotope concentrations may be calculated, however, if the R value (in equation 2.1) of the reference is known accurately. The choice of reference standards will be considered in section 2.2.4(c).

2.2.4(b) Algebraic manipulations in δ-notation

Four important algebraic manipulations using the δ-scale may be noted (from CRAIG, 1957, DARLING & BATH, 1979; GONFIANTINI, 1981):-

(1) Isotopic ratios may be compared through common measurement with respect to a material, m, by:-

$$\delta_{x-y} = \delta_{x-m} - \delta_{y-m} \quad \left(\frac{1000 + \delta x-m}{1000 + \delta y-m}\right) \quad {}^{o}/_{oo} \qquad (2.2)$$

where x and y are samples under investigation. This reduces simply to:-

$$\delta_{x-y} = \delta_{x-m} - \delta_{y-m}$$

where $\delta x-m$ and $\delta y-m$ are small in comparison with 1000. GONFIANTINI (1981) notes that this condition is more often satisfied for oxygen isotopes than for hydrogen, since in the latter case the δ-values are frequently one order of magnitude larger.

(2) The equation which reverses the usual δ expression, to give a reference value with respect to a sample is as follows:-

$$\delta_{m-y} = \left(\frac{1000}{1000 + \delta\, y-m} - 1\right) \times 1000 \quad {}^{o}/_{oo} \qquad (2.3)$$

(3) To convert the δ-value of a sample x which has been measured relative to a reference m, into another δ value relative to a second reference y, and where the first reference has been measured against the second, we may derive from equations (2.2) and (2.3) the following:

$$\delta_{x-y} = \delta_{x-m} + \delta_{m-y} + \left(\frac{\delta_{x-m} \times \delta_{m-y}}{1000}\right) \quad {}^{o}/_{oo} \qquad (2.4)$$

(4) A convenient property of the δ-notation (GONFIANTINI, 1981) is that the δ-value of a water sample, δs-m, which has resulted from the mixing of n different waters, each with isotopic composition δ_{x_i-m} is given by

$$\delta_{s-m} = \sum_{i}^{n} x_i \delta_{x_i-m} \qquad (2.5)$$

where x_i is the fraction of water corresponding to the ith component.

2.2.4(c) The reference standard: SMOW

For the intercomparison of stable isotope (H and O) results from different laboratories, an international standard water has been introduced with respect to which δ (${}^{o}/_{oo}$) results are normally reported. The reference standard is termed Standard Mean Ocean Water (SMOW). This

> "...corresponds to a hypothetical water having both oxygen and hydrogen ratios equal to the mean isotopic ratios of ocean water..." (GIONFIANTINI, 1981, p.37).

The choice of an ocean water as a standard is logical in terms of the importance of this reservoir in the hydrological cycle representing 97 to 98% of water in the hydrosphere (FONTES, 1976) and its apparent isotopic homogeneity (see section 2.3.2 (a)).

The isotopic ratios of hypothetical SMOW were first defined by CRAIG (1961b) with respect to an existing water standard provided by the National Bureau of Standards (NBS-1). In 1967, Craig was responsible for the

collection and isotopic adjustment of a large water sample, aiming to provide an isotopic composition as close as possible to that of the previously defined SMOW. This water has been distributed as a reference standard, called VIENNA-SMOW (or V-SMOW). For practical purposes, its isotopic composition is taken to be identical to SMOW (GONFIANTINI, 1978), defined as having values $\delta\,^{18}O_{SMOW} = 0\ ^{o}/oo$ and $\delta D_{SMOW} = 0\ ^{o}/oo$, and is the reference water used in this study.

Absolute isotopic abundance ratios in V-SMOW have been determined to be equal to $(155.76 \pm 0.05) \times 10^{-6}$ for D/H (HAGEMANN et al., 1970) and $(2005.20 \pm 0.45) \times 10^{-6}$ for $^{18}O/^{16}O$ (BAERTSCHI, 1976).

Other water samples distributed by the International Atomic Energy Agency (IAEA), and by the United States National Bureau of Standards, are listed, together with their isotopic compositions relative to SMOW by GONFIANTINI (1981).

Of these samples, SLAP (Standard Light Antarctic Precipitation) has been most widely used, providing an end member on a SMOW-SLAP scale.

Wherever $\delta^{18}O$ or δD values are given in this study, without mention of the reference water, it may be assumed that measurements are reported with respect to SMOW.

2.2.5 Isotopic Fractionation

2.2.5(a) The physical and chemical effects of isotope substitution

Substitution of isotopes in a molecule of water affects the properties controlled directly by molecular mass, such as specific gravity and molecular diffusivity. Examples of the differences in physical attributes of isotopic water species are given in table 2.1 and are discussed in detail by GAT (1981b) and by KIRSCHENBAUM (1951). The additional energy required by the heavier isotopes to undergo phase changes in the direction of solid through liquid to vapour result in the preferential 'escape' of the lighter isotope with the remaining mixture being relatively enriched in the heavier isotope.

With the reversal of phase changes, the heavier isotopes are the first to enter the lower energy state. Early workers exploited such differences in vapour pressures of isotopic water species to isotopically enrich their samples, and ultimately, to produce "heavy water", D_2O (SILVERMAN, 1951).

The density ratios of $H_2{}^{18}O$ and D_2O to 'normal' water ($H_2{}^{16}O$) are very similar to mass ratios, this being due to the virtual invariance of interatomic distances under isotopic substitution (GAT, 1981b). With the same configuration of electrons, the isotopes may form covalent bonds interchangeably with other nuclides. Such isotopic substitution, however, affects the vibrational state of the bond, and thus the equilibrium distribution of isotopes between water and other compounds is not uniform (GAT, op. cit.). Such factors contribute to the process of isotopic fractionation.

2.2.5(b) The terminology of fractionation

The partitioning of isotopes between two substances with different isotope ratios is termed isotope fractionation (HOEFS, 1973). This effect is largely responsible for the distribution of stable isotopes between natural materials as, for example, exemplified for oxygen-18 in fig. 2.2.

The isotope fractionation factor (α) between two substances, A and B, is defined as the ratio of their respective isotopic compositions (R_A and R_B), thus:

$$\alpha_{A-B} = \frac{R_A}{R_B} \qquad (2.6)$$

In δ notation, this expression becomes:-

$$\alpha_{A-B} = \frac{1 + \frac{\delta_A}{1000}}{1 + \frac{\delta_B}{1000}} = \frac{1000 + \delta_A}{1000 + \delta_B} \qquad (2.7)$$

where δ values are measured with respect to the same reference.

Fractionation factors are normally close to unity, typically 1.00x (ie. with a value x in the third decimal place). An alternative expression is in

terms of the per mil fractionation (ε), defined by

$$\varepsilon_{A-B} = (\alpha_{A-B} - 1) \times 1000 \quad {}^{o}/_{oo} \qquad (2.8)$$

Thus ε will be negative if α is less than one, ε will be positive when α is greater than one and when $\alpha = 1$ and $\varepsilon = 0$ there is no detectable difference in the isotope composition of the two substances under investigation. As an example, at $20^{o}C$ in a calcite-water exchange reaction for $\delta^{18}O$,

$$\alpha_{CaCO_3 - H_2O} = \frac{1.030}{1.000}, \text{ then } \varepsilon_{CaCO_3 - H_2O} = +30 \quad {}^{o}/_{oo}$$

indicating a relative enrichment of heavy isotopes in the $CaCO_3$ molecule, with respect to the water.

If natural logarithms are taken (denoted ℓn) of a fractionation factor (α) we may make use of the approximation

$$10^3 (\ell n\ 1.00x) \simeq x \qquad (2.9)$$

From Equ.(2.8)

$$\varepsilon_{A-B} \simeq 10^3 \ell n \alpha$$

Substituting equ. (2.7) also,

$$10^3 \ell n \alpha \simeq \delta_A - \delta_B \qquad (2.10)$$

That is, subtraction of δ values will be an excellent approximation to the per mil fractionation and identical to it within analytical error when values of both $(\delta_A - \delta_B)$ and individually δ_A and δ_B are within the limits of ± 10. This approximation is commonly applicable in considerations of $\delta^{18}O$ fractionation, but for δD fractionation, differences in $\delta_A - \delta_B$ are often an

order of magnitude greater, and therefore care must be taken in comparisons of declared fractionations. Examples of $\delta_A - \delta_B$ values and the associated $10^3 \ln\alpha$ values are presented in table 2.2 (from FRIEDMAN & O'NEIL, 1977) to illustrate the magnitude of these approximations.

The main phenomena producing the isotope fractionation effects may be divided into equilibrium and non-equilibrium processes, and these will be examined next. Additional phenomena which may lead to isotope fractionation will be considered briefly in section 2.2.5 (e).

2.2.5(c) Isotopic fractionation in equilibrium processes

Equilibrium processes are defined here as reactions in which reactant and product remain together so that continuing exchange of isotopes is possible, ie. so that a thermodynamic equilibrium may be established. In the natural environment, this may be viewed as a "closed system". Fractionation will be considered in terms of isotope exchange reactions among chemical species and in terms of differences produced at a change of phase.

Isotope exchange reactions

For the simplest case, we may consider an isotope exchange reaction in which ordinary changes in the chemical system do not occur, but in which the isotope distribution changes between different chemical substances. A typical reaction may be written:-

$$a\ C_1 + b\ D_2 \rightleftarrows a\ C_2 + b\ D_1$$

where C_1, C_2, D_1 D_2 are molecules which include isotopes of the same element, subscripts 1 and 2 referring to the light and heavy isotopes respectively. Examples of such reactions are given on the next page.

$$^{16}O_2 + 2H_2{}^{18}O \rightleftarrows {}^{18}O_2 + 2H_2{}^{16}O$$

$$C^{16}O_3^{2-} + 3H_2{}^{18}O \rightleftarrows C^{18}O_3^{2-} + 3H_2{}^{16}O \qquad (2.11)$$

If the isotopes are randomly distributed in the reacting compounds under equilibrium conditions the fractionation factor (α) is related to the equilibrium constant of the reaction (K) by:

$$\alpha = K^{\frac{1}{n}}$$

where n is the number of atoms exchanged and $K = \alpha$ in a monatomic reaction.

The fractionation factor is defined by the quotient of isotopic ratios in the respective species (HOEFS, 1973; FERRONSKY & POLYAKOV, 1982) thus for equ. (2.11):-

$$\alpha = \frac{(^{18}O/^{16}O)_{CO_3^{2-}}}{(^{18}O/^{16}O)_{H_2O}} \qquad (2.12)$$

The partitioning of isotopes between molecules in such a reaction may be calculated theoretically from statistical mechanics, but the majority of fractionation factors of geochemical interest, presented in the summary by FRIEDMAN & O'NEIL (1977), have been determined experimentally.

An example of the temperature dependence of the equilibrium fractionation factor (expressed as $10^3 \ell n\alpha$) is given in fig 2.4 for an equilibrium exchange of oxygen isotopes between carbon dioxide and water. At low temperaures, the fractionation is seen to increase, with ^{18}O being enriched in the carbon dioxide. At higher temperatures, the difference becomes smaller, increasing concentrations of ^{18}O being found in the water. The nature of this fractionation has particular relevance to the preparation of water samples for oxygen isotope analysis, to be described in section 3.4.1.

Phase changes

Fractionation in equilibrium conditions may take place at a phase change, between solid, liquid and/or gaseous forms of a particular substance. In addition to the previous definition of the fractionation factor (α), for the case of oxygen isotopes in water vapour in equilibrium with liquid, it can be shown that:

$$\alpha_{\text{water }(\ell)\text{-vapour}} = \frac{\text{vap press } (H_2{}^{16}O)}{\text{vap press } (H_2{}^{18}O)}$$

where $\alpha > 1$ since $H_2{}^{16}O$ is the more volatile water species. An example of such closed system, equilibrium fractionation is shown schematically in fig. 2.5.

The temperature dependence of deuterium and ^{18}O isotope fractionations between water and vapour, and ice and vapour, is illustrated in fig. 2.6. On evaporation or sublimation it may be seen that the vapour phase is relatively depleted in ^{18}O, but with increasing energy, provided by an increase in temperature, more of the heavy isotopes may escape into the vapour phase, and isotopic differences are reduced. With equilibrium condensation or freezing, the process is reversed, the heavier isotopes tending to form the lower energy states of liquid water or ice. An exception to this rule is found in hydrogen isotope exchanges at high temperatures, above 200°C, (MERLIVAT et al., 1963; BOTTINGA, 1968). For temperatures below 200°C, however, the fractionation of D parallels that of ^{18}O in most cases, since the physical processes responsible are the same (HOEFS, 1973). It is of note that fractionations in D are relatively larger, and further examples of the factors are given below.

Examples of equilibrium isotopic fractionations

Table 2.3 gives examples of experimentally derived fractionation factors under different equilibrium conditions. By way of example, at 20°C, the fractionation factor of ^{18}O between water in the liquid and water in vapour phase at equilibrium is 1.0098; thus the liquid phase is enriched in the ^{18}O by 9.8 °/oo relative to the vapour phase.

In addition to temperature dependence, fractionation is affected by the concentration of ionic species in water (GAT, 1981b). Such effects are considered small for ^{18}O compared to those on D, and may be negligible for both isotopic species in the low ionic concentrations frequently found in precipitation, surface waters and non-saline groundwaters. Exact thresholds of concentrations at which the effects may become important depend upon the ionic species present and are examined by SOFER & GAT (1972).

2.2.5(d) Isotopic fractionation in kinetic processes

Kinetic processes are those which are dependent upon the speed of a reaction, where equilibrium is not allowed to be established, and the composition of the flux of matter leaving a phase is not in thermodynamic equilibrium with the residual material. This is a common feature of many physico-chemical and isotopic systems. Kinetic isotope effects are seen where reactants or products of a process are removed before an equilibrium fractionation is established. In the natural environment, this may be termed an "open system".

The kinetic factor in fractionation may enter into both isotope exchange reactions and change of phase processes. Additionally, a well-mixed reservoir of isotopic species may undergo fractionation as a result of kinetic processes where no reactants are involved. An example is the diffusion of gas molecules, where molecules containing the light isotope move more rapidly than those with the heavy isotope; this source of fractionation

becomes important in the handling of gases which contain a mixture of isotopic molecules. Examples of the removal of reactants before an equilibrium is established are the incomplete acidification of a carbonate (a possible problem in sample preparation; FRIEDMAN & O'NEIL, 1977) and the evaporation of water into non-saturated air where removal is by molecular diffusion (GAT, 1981c).

The occurrence of kinetic processes in environmental conditions, for example with the exposure of lake surfaces to the atmosphere, is very important in the present work and therefore merits further discussion.

In laboratory experiments by CRAIG et al. (1963) and by others reported in GAT (1981c), it was found that water evaporating into dry air produced a greater isotopic enrichment than expected. This excess of the observed fractionation, α_o , above that expected for equilibrium conditions, α_e , is denoted by the kinetic separation factor, $\Delta\varepsilon$ (GAT, 1980; GILATH & GONFIANTINI, 1983):

$$\Delta\varepsilon = \alpha_o - \alpha_e \qquad (2.13)$$

In a consideration of equilibrium evaporation (as presented in section 2.2.5(c)), CRAIG et al. (1963) expected the relationship between $\delta^{18}O$ and δD to be given by $\varepsilon_D^*/\varepsilon_{18_O}^*$ where $\varepsilon^* = (1-1/\alpha)$. This ratio in ε^* may be calculated from data presented in table 2.3, and is found to be 8.0 at 20^oC for the liquid-vapour equilibrium. Similar figures were obtained by CRAIG et al. (1963) using early vapour pressure data for the hydrogen isotopic species of water, and by careful experimental determination of $\varepsilon_{18_O}^*$. Importantly, this value of 8 will be shown to be the slope of the $\delta^{18}O$-δD relationship in meteoric waters (section 2.3.2(b)). In laboratory and open-air experiments, however, the slope was found to be significantly lower than 8, falling in the range 3 to 6. DANSGAARD (1964) noticed a similar effect, and suggested a

molecular mechanism to explain the greater sensitivity of the oxygen-18 component, relative to the deuterium, to kinetic effects.

Further experimental work investigated the mechanics of kinetic fractionation in evaporation, GAT (1980) summarised the relationship of $\Delta\varepsilon$ to the key parameter of relative humidity, h (normalised with respect to saturated vapour at a specified temperature), as $\Delta\varepsilon$ being equal to $15(1-h)^{o}/oo$ for ^{18}O and $13(1-h)^{o}/oo$ for D. It is noted that the numerical values of $\Delta\varepsilon$ for a given humidity are rather similar for the two isotope species, but the significance in the contribution to the total observed enrichment, ε^{*}_{O}, is much greater for oxygen-18 than for deuterium. The lowering of the slope in the $\delta^{18}O$-δD plot due to kinetic effects is shown in fig. 2.7 from evaporation experiments performed by GILATH & GONFIANTINI (1983). The lowering of the slope is of particular importance in environmental investigations since from such evidence, kinetic evaporation of a water parcel may be inferred.

An example of an open system is shown in fig. 2.8(a) and (b). Aliquots are taken for isotopic measurement from the reactant and the product reservoirs, and equilibrium fractionation not found between them, in contrast with fig. 2.5.

In the open system, water vapour (δ_b) forms above a liquid reservoir ($\bar{\delta}_a$), in instantaneous equilibrium, but is removed from the system and further equilibration is prevented, as the vapour is added to the reactant reservoir ($\bar{\delta}_b$). A similar situation may occur in the formation from a water body of water vapour, which subsequently precipitates. In such a system, the following mass balance equation is valid (FRITZ & FONTES, 1980):-

$$f(\bar{\delta}_a) + (1-f)\bar{\delta}_b = \delta^{o}_a$$

where δ^{o}_a is the original isotopic composition of the reactant reservoir, and

f is the residual fraction of reactant at any moment. By integration, the instantaneous isotopic composition of the product, the isotopic composition of the changing reactant reservoir and of the product reservoir may be computed (fig. 2.8(b)).

Importantly, similarities are found in the modelling of in-cloud condensation of water which may be viewed as a quasi-kinetic process.

Both open and closed condensational systems may occur in nature with additional complications of temperature changes during condensation and also re-evaporation. These will be considered in more detail when atmospheric moisture is examined in section 2.3.2.

2.2.5(e) Interaction of isotopes with materials of the natural environment

The natural fractionating mechanisms examined briefly below are expected to be of minor importance in this study. An attractive feature of the stable isotopes for hydrological studies is that they behave as 'conservative tracers', having only limited interaction with the media through which they pass (at normal temperatures and pressures).

Low temperature mineral-water interaction (0 - 50°C)

Slow processes of diffusion and exchange between waters and minerals at low temperatures have been considered by certain workers to produce fractionation over the long term, but FONTES (1976) refers to these

> "phénomènes d'ultrafiltration" as "... effets mal connus et de toutes façons relativement limités" (p.210).

SAVIN (1980) agrees that isotopic exchange at 'sedimentary' temperatures is slow, noting in addition that (p. 283)

> "... in most surface and near surface environments, the amount of water is much larger than the amount of exchanging solid phase, and the isotopic composition of water is therefore not measurably altered on a local scale".

This qualitative statement supports the argument for the stable isotopes of oxygen and hydrogen behaving as conservative tracers.

High temperature mineral-water interactions

Characteristic isotopic alteration of waters encountering minerals at high temperatures (say $>350^{o}C$) has encouraged the development of isotope hydrology in geothermal systems, a large subject area reviewed elsewhere (TRUESDELL & HULSTON, 1980; PANICHI & GONFIANTINI, 1981). Processes of equilibrium fractionation significantly enrich the $^{16}O/^{18}O$ composition of meteoric waters through isotopic exchange with the rocks constituting the geothermal reservoir. The D/H ratio is little affected, and fig. 2.9 shows the characteristic plot of such waters on a $\delta^{18}O$-δD diagram. Although bringing significant benefits to the study of geothermal systems this aspect will not be examined further in the present study. It is noted, however, that studies of hydrology in the geothermal areas in the U.K. may benefit from this labelling of stable isotopes.

Biological processes

It is generally considered that the uptake of water by plant roots is not a fractionating process. Subsequent photosynthesis and respiration does, however, result in fractionation of the isotopes of oxygen (in both processes) and hydrogen (in photosynthesis only) (HOEFS, 1973). FONTES (1976) notes that transpiration from vegetation results in kinetic fractionation of water, giving a $\delta D/\delta^{18}O$ slope of ~ 3, which is comparable to the effects of evaporation from open water surfaces, discussed earlier. The timing of water uptake by plants, with respect to isotopic input variations in recharge is expected, however, to have a greater isotopic impact on recharging water in the present scale of study, rather than any biological fractionating processes.

2.3 Stable isotope variations in the hydrological cycle

2.3.1 Introduction

Fractionation effects are the principal cause of variations in

stable isotope composition both within and between components of the hydrological cycle, the latter being presented schematically in fig. 2.10. Isotopic variations in components have been detected over a range of scales in time and space. In this section, investigations into the driving mechanisms of these variations will be presented.

Variations in the isotopic input signal of precipitation are of most significance in the use of the isotopes of hydrogen and oxygen as 'natural tracers' in hydrology. The nature of this input, therefore, merits detailed consideration (section 2.3.2). Terrestrial modification of the isotope input signal will be examined in section 2.3.3.

2.3.2 Isotope signals in meteoric waters

2.3.2(a) Ocean water - the source of atmospheric moisture

Ocean waters play an important role in the cycling of isotopes of oxygen and hydrogen in the hydrosphere, since they may be viewed as the starting and end points of the cycle, and represent a relatively large reservoir of the total water available for cycling.

DANSGAARD (1964) notes, from the co-ordinated and original work performed by EPSTEIN & MAYEDA (1953) and by FRIEDMAN (1953), that the oceans have "... a fairly uniform isotopic composition disregarding those parts which are directly mixed with fresh water." (p.436). This uniformity is found predominantly in deep (>1000 m) ocean waters, which represent 75% of all ocean waters by mass, according to FERRONSKY & POLYAKOV (1982). Surface layers are subject to local and regional variations, mostly as a function of evaporation (causing isotopic enrichment of the ocean water) as a function of the input of meteoric waters, and as a function of exchange with atmospheric CO_2 (a minor process resulting in ^{18}O depletion of the ocean water; BOTTINGA & CRAIG, 1969). MAGARITZ & GAT (1981) report that isotope variations within the oceans do not normally exceed $\pm$ 2 $^{o}/_{oo}$ in $\delta^{18}O$. A mean $\delta^{18}O_{SMOW}$ value for ocean surface waters was estimated by Craig (reported in MAGARITZ & GAT,

op cit.) to be +0.5°/oo. Parallel variations in δD values were found by FRIEDMAN (1953), with the slope of the line $\delta^{18}O$ against δD approximately equal to 8; FERRONSKY & POLYAKOV (1982) report a less steep slope for evaporating surface waters, in accordance with the kinetic fractionation processes discussed in section 2.2.5(d).

The importance of the reported relative isotopic homogeneity of ocean waters lies in it being the major source of atmospheric water vapour. Evaporation from the ocean surfaces has been investigated in detail by Craig & Gordon (in 1965; reported by YURTSEVER & GAT, 1981, and by FERRONSKY & POLYAKOV, 1982). In a North-South traverse of the Pacific Ocean, values of $\delta^{18}O$ in water vapour (collected at ship's mast height) plotted against latitude, show significant discrepancies from an equilibrium isotopic value in water vapour, calculated from sea surface $\delta^{18}O$ and temperature values. Such discrepancies are greatest in the latitudes where the trade winds dominate (eg. 5-25 °N), the measured water vapour being 4.5 °/oo lighter ($\delta^{18}O$) than expected from equilibrium fractionation. Similar observations were made for δD by KOWSKI et al. (1982) in a traverse of the Atlantic Ocean. It is concluded that kinetic fractionation is taking place, controlled by processes of molecular diffusion between the evaporating surface and the layer of well-mixed turbulent air above.

Much more emphasis in the study of isotopes in meteoric waters has been placed on the condensation process than on the initial evaporation; the only inclusion of water source in many precipation models is in terms of distance travelled by the advancing air mass. SEIGENTHALER & MATHER (1983), however, argue that consideration of sea surface temperature and relative humidity at vapour source (as well as at the site of meteoric water collection) should be included in future, more detailed, modelling of isotopic input as precipitation.

2.3.2(b) Stable isotopes in meteoric waters: monthly monitoring of isotope 'effects'

Introduction

Early exploratory studies of the distribution of stable isotopes in natural waters included analyses of precipitation samples from many parts of the world (EPSTEIN & MAYEDA, 1953; FRIEDMAN, 1953; DANSGAARD, 1953). The existence of a statistical, linear relationship between $\delta^{18}O$ and δD in meteoric waters was first presented by CRAIG (1961a) to be:-

$$\delta D = 8\,\delta^{18}O + 10 \qquad (2.14)$$

This locus of isotopic composition, referred to as the 'Meteoric Water Line' (MWL) and shown in figs. 2.7 and 2.9, was also found to fit many fresh-water sources, which were derived from meteoric waters, and provided impetus for further studies.

Investigations into the statistical relationship of isotopic input in precipitation with meteorological conditions were greatly assisted by the establishment of a worldwide precipitation network, organised jointly by the International Atomic Energy Agency (IAEA) and the World Meteorological Organisation (WMO), in 1961. This network, of originally 144 meteorological stations but now reduced to 65 stations, is organised to collect precipitation samples on a monthly basis for isotope analysis. An excellent framework is provided for the basic quantification of worldwide stable isotope characteristics in precipitation. Initial results from the network were examined, for 1961 and 1962, by DANSGAARD (1964). In this classic paper are identified four isotope "effects": the temperature, amount, latitude and altitude effects. Additionally, the nature of $\delta^{18}O$-δD relationships and the seasonality of isotope signals in precipitation are explored. The importance

of DANSGAARD'S paper is twofold:-

(a) it summarises the statistical patterns of isotope variations observed in monthly precipitation samples and relates these to meteorological and geographical parameters; and

(b) it suggests a theoretical framework for the observed characteristics of isotopes in meteoric waters.

The framework proposed was that of a 'Rayleigh distillation' process which was subsequently used by many workers, and a brief description of which is included in this section. To follow, a review will be presented of the theoretical background and the empirical evidence found by various workers for the isotope effects, $\delta^{18}O$-δD relationships and isotopic seasonality previously mentioned. Discussion of comparable properties in short-period precipitation events (at the timescale of less than one month) are reserved until section 2.3.2(e).

The utility of the expression of isotope effects and other properties in meteoric waters lies in their use for making preliminary estimates of isotopic values in precipitation where actual data do not exist (YURTSEVER & GAT, 1981), as well as in aiding attempts to relate the isotopic record, preserved in a variety of materials, to climates of the past (palaeoclimates). In terms of natural tracing studies in hydrology, understanding of the input signal in precipitation is essential for efficient research design and for proper interpretation of the output isotopic signal in ground and surface waters. Such understanding holds important implications as to the suitability for tracing studies of a particular area, since without a definable isotopic input signal, the study may be totally impracticable.

The Rayleigh distillation model

DANSGAARD (1964) considered that "... most important for the isotopic composition of precipitation is the condensation" (p.439). He applied a Rayleigh model to describe the process of slow condensation, with instantaneous isotopic equilibrium between the two phases, and with immediate removal of the condensate from the vapour after formation.

The first small amount of water condensed from vapour in equilibrium with SMOW (ie. with ocean water) would have the same composition as SMOW (reversing the fractionation incurred in evaporation). With further condensation the vapour preferentially loses the heavy isotopic components, and so δ_v of the remaining vapour, and consequently δ_c of the newly formed condensate become progresively negative (relative to SMOW), as indicated in section 2.2.5(d).

In studies proposing the physical explanation of an observed isotopic composition in precipitation, the Rayleigh model has been almost exclusively used. The equations which describe the changing isotopic composition of the vapour from which water condenses are given by FRITZ & FONTES (1980, p.34) The most important of these describes the isotopic compositon of the instantaneously formed condensate (δ_c):-

$$\delta_c = \delta_o \quad (\bar{\alpha}_e - 1) \ln f \qquad (2.15)$$

where δ_o is the initial vapour isotopic composition, $\bar{\alpha}_e$ is the mean equilibrium fractionation factor and f is the fraction of vapour remaining, relative to the initial amount. For the case of isothermal condensation, ie. with no change in temperature, a situation directly comparable with the case of 'open system' evaporation, as examined in section 2.2.5(d), is seen. Fig. 2.11, however, plots the change in $\delta^{18}O$ isotopic composition, against the

fraction of vapour remaining (f), with cooling of the air mass from a 10°C dew point to 0°C. The Rayleigh model (line A) is compared with the composition of liquid water in a closed system (no rainout) (line B) and with the hypothetical evolution of precipitation on passage over a mountain chain, with buildup and then dissipation of clouds (after GAT & DANSGAARD, 1972; FRITZ & FONTES, 1980).

DANSGAARD (1964) openly admitted the gross simplifications made in the application of the Rayleigh distillation model. It was seen as an extreme case in a spectrum of possible condensation scenarios. The opposite end-member would be the model of continuous isotopic equilibrium between two phases. Craig and Gordon (1965; reported in YURTSEVER & GAT, 1983) proposed an intermediate model. In this, equilibrium between vapour and condensate was allowed to exist for a limited period, before removal of the condensate from the system. This refinement brought small quantitative improvements in prediction, but qualitatively represented a very similar method of fitting a simple model to averaged isotopic and climatic data.

In such models, the effects of cooling, which is the normal mechanism producing condensation in the atmosphere, are of prime importance; attempts are made to match theory with the empirically observed "temperature effect".

The temperature effect

The temperature effect describes the increase in isotopic enrichment in precipitation observed with increased (air) temperatures. To explain this empirical observation, DANSGAARD (1964) applied the Rayleigh model. He described variation in the fractionation factor, α_e (equation 2.15), with temperature t°C, and computed δ_c and δ_v values for defined cooling temperatures below specific dew point temperatures. It is predominantly the process of progressive cooling associated with more complete progressive rainout which produces the effect of lower (more negative) isotopic values in precipitation produced at lower temperatures, rather than the temperature

dependence of α_e. Processes of both isobaric (constant volume) cooling and moist-adiabatic (expansion with) cooling were evaluated by DANSGAARD in such a two-phase (vapour-condensate) system for the isotopes of oxygen and hydrogen. Examples of DANSGAARD's calculations are shown in table 2.4.

A great sensitivity of condensate (instantaneously formed) to temperature is seen with a lower initial (dew point) temperature, and with isobaric cooling rather than with moist-adiabatic cooling. Despite the great simplifications in condensation dynamics implicit in the Rayleigh model, a reasonable agreement was found between the predicted relationship $d\delta^{18}O/dt$ and the slope of the observed relationship between annual $\delta^{18}O$ in precipitation and the mean surface air temperatures for North Atlantic coastal stations and the Greenland ice cap (examined in more detail below). Both slopes were of the order of 0.70 $^{o}/oo/^{o}C$. The gradient calculated using the Rayleigh model was actually 0.67 $^{o}/oo/^{o}C$, and assumed cooling to be initially by isobaric processes (from dew point at $20^{o}C$ to $0^{o}C$) and then by moist-adiabatic processes (to $-20^{o}C$).

Turning attention to empirical studies, SEIGENTHALER & MATHER (1983) noted that three approaches were possible in the analysis, with respect to temperature, of $\delta^{18}O$ values in precipitation, from a monthly monitoring network, viz. examination of:-

(1) Changes of annual mean values at a fixed location;

(2) Annual mean values at different stations;

(3) Short-term (seasonal) variations at a fixed location.

In general, inadequate data are available over periods of several years to determine the influence of trends in circulation patterns, as would be revealed by (1), and more commonly variations in space, as in approach (2), are substituted for variations through time, in investigations of the

temperature effect. This is a good example of the ergodic principle, replacing time with space (HARVEY, 1969, p.128). This second approach will be discussed briefly below. The factor of stable isotope seasonality in precipitation at particular locations, approach (3), above, will be dealt with separately in section 2.3.2(d), due to its importance in studies using environmental isotopes as natural tracers.

Most commonly, in expressions of the global "temperature effect", mean annual temperature values at ground level are substituted for condensation temperatures. Commenting on the simple linear relationship assumed between such values, FONTES (1976; p.208) considers that this substitution is only satisfactory at such a level of averaging (through time) that the meteorological anomalies which frequently accompany precipitation events (such as temperature inversions, development of convective circulation cells, frontal occlusions, etc.) are smoothed out. For this reason, mean annual temperatures may be used more successfully in expression, of the temperature effect, than measurements at higher levels of resolution.

The classic pattern of the global correspondence between $\delta^{18}O$ values in precipitation and mean annual temperatures, as previously mentioned, was presented by DANSGAARD (1964) for stations fringing or within the Atlantic Oceans (North and South). The plot of stations is shown in fig. 2.12, and the following empirical relationship was found:-

$$\delta^{18}O_a = 0.695\ t_a - 13.6\ ^{o}/_{oo} \qquad (2.16)$$

where t_a is the mean annual temperature and $\delta^{18}O_a$ is the mean annual oxygen-18 value in precipitation. The above relationship applied best to stations having mean annual temperatures less than $10^{o}C$. It is to be noted from fig. 2.12 that deviations from this relationship are significant: island stations tend to lie above the computed regression (isotopically

heavier), and more 'continental' stations below the line (isotopically lighter). DANSGAARD explained the apparent displacement of Antarctic precipitations, from the general relationship, as being due to the relatively warm South Atlantic providing isotopically heavier water vapour, and a greater complexity of air mass paths of travel compared with the northerly situation.

Data from all the reporting stations in the IAEA/WMO network are examined by YURTEVER & GAT (1981), who find a smaller gradient for the temperature effect in $\delta^{18}O$ in comparison with equation (2.16), viz:-

$$\delta^{18}O_a = (0.338 \pm 0.028)t_a - 11.99\ ^{o}/_{oo}$$

91 stations, were included and a correlation coefficient, r, of 0.79 was found. This change in gradient is due to the inclusion of stations where the isotopic input is less sensitive to temperature. DANSGAARD (1964), found this to be the case especially for tropical stations.

An intermediate temperature effect was found by van der STRAATEN & MOOK (1983) for stations within the average annual temperature range $0^{o}C < t_a < 18^{o}C$, ie. in mid-latitude locations, of the form (p.60):-

$$\delta^{18}O_a = (0.56 \pm 0.09)t_a - 12.7\ ^{o}/_{oo}$$

Again, agreement could be found between this empirical value and a proposed model of simplified Rayleigh distillation, in this case from an equatorial source with annual average temperature of $25^{o}C$.

One must assume, with so many variables applied in even a simplified model of the distillation process, that intelligent reconstruction of the empirical temperature effect is reported by these and other workers (eg. SONNTAG et al., 1983), rather than the remarkable resilience of the Rayleigh

model to produce similar results within the variety of conditions specified by each author.

The 'amount effect': In-cloud processes and isotopic alteration of falling raindrops

Empirically an inverse relationship between precipitation amount and stable isotope δ values has been observed in data collected in the IAEA/WMO monthly monitoring network.

DANSGAARD (1964) considered the effects of the degree of rainout from clouds and processes of exchange between, and evaporation from, raindrops (condensate) and their surrounding vapour. Three factors may be noted which would bias heavy rainfalls to be associated with isotopically light water, and vice versa:-

(1) The integrated δ value of total condensate produced will lower (become more negative) with a proportional increase in rainout from the cloud (viewed as the water vapour reservoir). SIEGENTHALER & MATHER (1983) note that (p.39)

> " ... the direct influence of temperature on the rainout of heavy isotopes is of minor importance only. There is a large indirect effect, because condensation is in general an effect of cooling, so the remaining fraction of vapour, f, is related to temperature."

Thus the more complete the rainout (generally associated with lower condensation temperatures), the lighter will be the sum of precipitation collected following line A of the Rayleigh model in fig. 2.11.

(2) Isotopic exchange with environmental vapour is more pronounced in light rain. Assuming the vertical profile of decreasing relative concentrations of heavy isotopes with altitude in the troposphere, as described by ROSANSKI & SONNTAG (1982), raindrops falling through the lower atmosphere will be subject to isotopic enrichment by isotopic exchange. This equilibrium process was verified under experimental conditions, in a vapour-saturated gas flow, by STEWART (1975).

(3) Evaporation from precipitation falling through unsaturated air tends to further concentrate heavy isotopic species in precipitation. An instantaneous kinetic fractionation, larger than the equilibrium fractionation, was found by STEWART (1975) between water droplets (at an estimated wet bulb temperature) and a dry atmosphere.

The increase in isotopic enrichment of rainfall with decreasing rainfall amounts, resulting from processes (1)-(3) is termed the 'amount effect' (DANSGAARD, 1964). Evidence of the effect is illustrated in fig. 2.13 for tropical island stations, for which DANSGAARD found the temperature effects to be of relatively minor importance. YURTSEVER & GAT (1981) computed the average rate of depletion in $\delta^{18}O$ to be 1.5 ± 0.2 °/oo/100 mm precipitation for this data set ($n = 14$, $r = 0.87$). In tropical regions, with a steady supply of moisture carried by the Trade Winds, the higher monthly rainfalls are reflecting higher than average removal of water from the air, resulting in precipitation more depleted in oxygen-18. Since the heaviest rain may fall in the warmer season, for a particular station, the trend of the normal temperature effect may be more than outweighed by the amount effect. In certain semi-arid climates, where the re-evaporation may be expected, no evidence of an amount effect is found simply because no rain falls in the dry season, to be recorded as 'isotopically enriched'.

Since solid precipitation is less susceptible to the processes of evaporation (or sublimation) and exchange, the amount effect in areas receiving mostly snowfall (or hail) would be due almost entirely to the completeness of 'rainout' within the clouds, and not to post-condensational processes.

The 'latitude effect'

The latitude effect refers to the general depletion of heavy isotopes (δ values becoming more negative) with increasing latitude, from equator to poles. Such broad global zonation was proposed after analysis of results

from the IAEA/WMO precipitation network, and is illustrated in fig. 2.14. Air temperature, as a surrogate of condensation temperature, decreases with increasing latitude, and largely contributes to this 'effect'. The amount effect may also contribute to the observed isotopic pattern if a single Hadley cell type circulation is envisaged, from equator to poles, with the first, isotopically heaviest, rainout occurring at low latitudes, and subsequent rainout at high latitudes being relatively isotopically depleted.

YURTSEVER & GAT (1981) evaluate the latitude effect to be approximately -0.5 $^{o}/_{oo}$/degree latitude, for $\delta^{18}O$ in precipitation over the North American continent. It is important to note, however, that the global model is a gross over-simplification of reality, and distortion of a strict latitudinal pattern over the continents is apparent (fig. 2.14). The resultant pattern is likened, by SONNTAG et al. (1983), to iso-lines of precipitable water, a global pattern of which was shown by REITAN (1960), and this is perhaps an appropriate comparison in view of the similar determining mechanisms.

The 'altitude effect'

Both the 'temperature effect' and the 'amount effect' contribute to the so-called 'altitude effect', which is the term used to describe the isotopic depletion observed with increasing altitude. Condensation which occurs at higher altitudes generally forms at lower temperatures and therefore produces isotopically lighter precipitation; also, rainout has frequently already occurred from the air mass at lower altitudes (depending on the geographical location of the high relief with respect to the source of water vapour, along the air mass trajectory), tending to reinforce the pattern, but being dependent upon the type of precipitation falling.

The altitude effect may be important in hydrological studies using stable isotopes as natural tracers, since it may provide, for example, a convenient 'label' on isotopic input values at different altitudes in the study area .

Precipitation may be grouped into four categories, according to the mechanisms of cloud formation. These are (McINTOSH, 1972):-

(1) cyclonic precipitation

(2) convective precipitation

(3) orographic precipitation

and (4) advective precipitation

Precipitation produced in category (4) is normally slight and is of little importance in this examination. Precipitation types (1)-(3) involve appreciable vertical motion in their formation and are associated with adiabatic cooling (in which heat does not enter or leave the system), whereas isobaric cooling (referring to temperatures along lines of equal pressure) may be applicable when considering horizontal variations of temperature between locations at the same altitude (and thus may relate better to the 'latitude effect').

SIEGENTHALER & MATHER (1983) compute, for a typical moist adiabatic lapse rate of $-0.53^{o}C/100$ m, and water vapour at $10^{o}C$ and 1000 mbar, a ($\delta^{18}O$) theoretical gradient of approximately 0.38 $^{o}/oo/^{o}C$. A gradient of 0.62 $^{o}/oo/^{o}C$ is computed by these authors for $\delta^{18}O$ variations with isobaric cooling, under comparable conditions.

The IAEA/WMO network provides little information concerning the altitude effect. The majority of stations are at or near sea level, only 20% being 500 m or more above sea level (YURTSEVER & GAT, 1981) and on the global scale this effect tends to be over-shadowed by the other isotopic effects previously discussed.

Examples of published gradients are given in table 2.5 which shows, for different geographical regions, that the magnitude of the effect depends on local climate and topography. Gradients in $\delta^{18}O$ of between -0.15 and $-0.5^{o}/oo/100$ m and gradients in δD of between -1.5 and -4 $^{o}/oo/100$ m are typical. Isotopic gradients have been measured over different time scales,

for example on a monthly basis by PAYNE & YURTSEVER (1974), or ZUPPI et al. (1974), and for a particular rainstorm for example, by Fontes & Olivry (reported in FONTES, 1976). Comparable orders of magnitude are normally reported for this effect, however, despite different measurement periods.

Summation of the effects: multiple regression analysis

Statistical manipulations of data from the IAEA/WMO network have been published extensively (DANSGAARD, 1964; IAEA, 1969, 1970a, 1971, 1973, 1975, 1979a; 1981b), and only a brief summary will be presented here.

Least squares regression of appropriate variables has been the most common technique employed for the summary of monthly or aggregated annual data. Thus, multiple linear stepwise regression was performed by YURTSEVER (1975; see also YURTSEVER & GAT, 1981) on monthly data from the IAEA/WMO precipitation network. The mean measured monthly isotopic composition, $(\overline{\delta^{18}O})_m$, was related to the basic climatological and climatic parameters by summation of the isotope effects using an equation of the form:-

$$(\overline{\delta^{18}O})_m = a_o + a_1 T + a_2 P + a_3 L + a_4 A$$

where T is the average monthly temperature (^oC), P is the average monthly precipitation (mm), L is latitude (degrees), A is altitude (in m above sea level) and a_o, a_1, a_2, a_3, a_4 are the respective regression coefficients. $(\overline{\delta^{18}O})_m$ denotes the arithmetic mean monthly oxygen isotope composition in precipitiation; alternatively, a mean $\delta^{18}O$ value weighted for monthly precipitation amounts may be used, $(\overline{\delta^{18}O})_{mw}$, computed as:-

$$(\overline{\delta^{18}O})_{mw} = \frac{\sum_{i=1}^{n} P_i \delta^{18}O_i}{\sum_{i=1}^{n} P_i} \qquad (2.17)$$

where subscript i denotes the month under consideration. The difference between this $\delta^{18}O$ value and that of the unweighted mean is not generally

significant for stations with a rather uniform monthly distribution of precipitation, but the weighted mean is expected to be the more appropriate index for tracer-input considerations in hydrological applications.

Using monthly averaged data from 91 network stations, YURTSEVER & GAT (1981) found partial correlation coefficients for $(\overline{\delta^{18}O})_m$ with temperature to be 0.815, with precipitation to be 0.303, with latitude to be -0.722 and with altitude to be 0.007. Problems of multicollinearity in the use of the chosen variables (eg. a strongly negative correlation being found between temperature and latitude) is discussed more fully in YURTSEVER (1975), but it remains that temperature is the only variable which correlates significantly with $(\overline{\delta^{18}O})_m$.

2.3.2(c) The $\delta^{18}O$-δD relationship in natural waters

The isotope effects discussed in the previous section have been concerned with the position of the isotopic composition of a particular parcel of precipitation along a locus of possible plots defining the $\delta^{18}O$-δD relationship, as summarised in fig. 2.15 for CRAIG's (1961a) empirically defined Meteoric Water Line (MWL).

The gradient of 8 of the MWL was found by DANSGAARD (1964) to have a sound physical basis. It is the $\delta^{18}O$-δD gradient of a vapour produced under equilibrium (or equally-counteracting kinetic) fractionating conditions and may be derived from the ratio of the appropriate isotopic enrichment factors (section 2.2.5(d)). The intercept in the equation of the MWL, not accounted for in equilibrium distillation, has been attributed to the kinetic effect of oxygen-18 fractionation by evaporation (ERIKSSON, 1983). To examine this phenomenon, DANSGAARD (1964) introduced the deuterium-excess (d-excess)parameter, where

$$\text{d-excess} \equiv \delta D_{SMOW} - 8\delta^{18}O_{SMOW} \qquad (2.18)$$

Waters falling on the Meteoric Water Line have (by definition) a d-excess value of 10. DANSGAARD argued that water undergoing equilibrium

processes will not change its value of d-excess, and therefore provided a useful characteristic of the water, for example, for hydrological studies.

The parameter describes the isotopic position of a particular water in relation to the MWL, but should not be confused with the expression of the intercept, since the locus of a particular water analysed may display a combination of slope and intercept different from that of the MWL. Fig. 2.16 illustrates a possible case, where water vapour (line Ve V_{n-e}) is produced with kinetic fractionation from a water body of limited size (line E, derived from SMOW). The resultant isotopic composition of meteoric water from this source is given by the locus through P, assuming equilibrium conditions of condensation. The magnitude of the d-excess parameter acquired is seen to be dependent upon the strength of the kinetic component in the evaporation process.

YURTSEVER & GAT (1981) find the following least-squares-fit linear relationship between annual weighted $\delta^{18}O$ and δD in precipitation, $(\delta^{18}O)_{aw}$ and $\overline{(\delta D)}_{aw}$, when all network IAEA/WMO stations are included:

$$\overline{(\delta D)}_{aw} = (8.08 \pm 0.8)\overline{(\delta^{18}O)}_{aw} + (9.57 \pm 0.62)$$

for n = 153, r = 0.995.

This is in good agreement with CRAIG's (1961a) Meteoric Water Line. Only very slight differences are found when unweighted averages are used or when figures representing stations are divided according to station climatic types of island/coastal/continental categories. When long term mean values of monthly precipitation ($\overline{(\delta^{18}O)}_{mw}$, $\overline{(\delta D)}_{mw}$) are examined however, and even more so, individual monthly values ($\overline{(\delta^{18}O)}_{m}$, $\overline{(\delta D)}_{m}$), patterns emerge in the isotope relationship which reflect regional climatic and meteorological factors. Long term data presented by YURTSEVER & GAT (1981) confirm the earlier findings by DANSGAARD (1964), who grouped stations according to the

slope and d-excess in the $\delta^{18}O$-δD relationship in monthly precipitation. The most significant groupings are summarised in table 2.6. Figure 2.17 shows schematically how these groupings might plot relative to CRAIG's MWL.

Slopes of less than 8 are most normally associated with re-evaporation of precipitation in warm and/or arid climates or seasons, and also with the very high net evaporation rates of Trade Wind islands. Since kinetic factors are most frequently associated with evaporative conditions (and not so frequently with condensation), the d-excess parameter is frequently taken to be an indicator of moisture source. Where the original source of water is an evaporated water body, a high d-excess is normally observed. A notable example is the d-excess of +22 $^{o}/oo$ found by GAT & CARMI (1970) for precipitation in the Mediterranean region.

2.3.2(d) Seasonal isotopic variations in precipitation

On the basis of the seasonality of controlling factors in the temperature and amount effects (ie. temperature regime, rainfall amount, relative humidity), and the variations in the source of precipitating air masses at a given location, it was anticipated by early workers that seasonality would be observed in the isotopic input signal. This encouraged the use of monthly precipitation monitoring, for adequate resolution of seasonal effects.

Several measures have been proposed as indices of isotopic variability in precipitation. The simplest is the range ($^{o}/oo$) of δ values between winter and summer, as used by DANSGAARD (1964), but the most useful index is probably that of the variance (σ^2, or standard deviation,σ) in monthly $\delta^{18}O$ and δD values, which are documented for network stations in YURTSEVER & GAT (1981) and IAEA (1969, 1970a, 1971, 1973, 1975, 1979a, 1981b), examples of which were provided in table 2.6.

Fig 2.18 clearly shows the larger variations in monthly $\delta^{18}O$ exhibited by continental stations relative to island stations for comparable monthly

mean isotopic concentrations. A larger seasonal spread of isotope values might be expected to be associated with a larger variance in temperature. This is indeed the case for stations within Group A in fig. 2.19 (note the log-log scale), island and coastal stations with small temperature variances, showing the weakest variations in $\delta^{18}O$. Significantly higher isotopic variances are found, however, in groups B and C, in comparison with equivalent temperature variances of Group A. This is attributed by YURTSEVER & GAT (1981) to amount effects primarily dependent upon rainout (group B) or re-evaporation from raindrops (Group C).

An example of the very strongly seasonal pattern of isotopic input in precipitation over Vienna is shown in fig. 2.20 together with monthly temperature data. In attempting to model seasonal isotopic variations, over continental Europe, ROSANSKI et al. (1982) found that, among other factors, the carry-over of winter precipitation contributing to summer evapotranspiration (which is subsequently precipitated) damped down seasonal patterns which might otherwise be expected from a model of single-source advection of water vapour.

YURTSEVER (1975) has analysed isotopic time series for indications of periodicity using auto-correlation and spectral analysis techniques. The majority of stations analysed revealed a 12-monthly cycle, which is not surprising in view of the evident annual seasonality and the limitations of using only 6 years of monthly data. Certain coastal and island stations, however (including Reykjavik, Tokyo and Hilo-Hawaii), were found to have no distinct cyclical variations in their $\delta^{18}O$ time series. Variations observed here were thought to be of a random character, relating to local climatological conditions and possibly the superimposition of weak isotopic effects upon one another.

HÜBNER et al. (1978) also used spectral analysis, in the examination of

monthly data from stations in East Germany. 12-month periodicity was again observed, but unfortunately, no attempt was made to reconcile this with the interesting tabulation in this study of δD values according to air mass types, for which a seasonal variation in vapour source and frequency of ocurrence had been noted.

2.3.2(e) Empirical studies of short period variations in the stable isotope composition of precipitation

In general, the 'isotope effects' were noted and developed from monthly observations, invoking the dynamic process of Rayleigh distillation only at an aggregated level. Short period investigations test the physical reality of such an approach. Surprisingly few studies of short period (<1 month sampling interval) variations of the stable isotope composition of precipitation have been carried out. Of those studies published, three categories may be recognised:-

(1) The examination of in-cloud processes. Records of such processes are only reliably kept, if ground level collection is used, by solid precipitation. Snow and hail have thus been studied (eg. by EHHALT, 1967; MACKLIN et al., 1970) and attempts made to relate measured isotopic values to models of multi-stage vertical distillation columns, which reflect the complexity of in-cloud dynamics.

(2) The examination of post-formation processes on precipitation. The dynamics of molecular exchange and evaporation from falling (liquid) precipitation are examined in more detail, notably by attempts to relate such processes to size of droplet or rainfall intensity, together with atmospheric conditions, eg. by WOODCOCK & FRIEDMAN (1973).

(3) The relating of short period variations of isotopes in precipitation to concomitant meteorological observations, with consideration of prevailing synoptic conditions. By identifying isotope patterns in precipitation

monitored at ground level, with factors such as air mass trajectories and positions with respect to fronts, an attempt is made to bridge the gap between the statistical expression of longer-period (eg. monthly) means and the detailed dynamics of atmospheric processes (as in (1) and (2)).

Studies in categories (1) and (2) may contribute much to the modelling and understanding of isotope variations in atmospheric waters. They also provide feedback of information to meteorology as a discipline, since the concept of 'natural tracing' may equally well be applied to atmospheric processes. Information from category (3), however, appears to be of more immediate use in hydrological applications in the terrestrial part of the water cycle. This is particularly the case where monitoring of input variations is required at a shorter than one month interval, due to the fast response of the system under investigation. YURTSEVER & GAT (1981), in justifying the global IAEA/WMO network of monthly collections note that (p.103)

> ".. individual rainfall events leave little impression on most hydrological systems because of the latter's size and inertia. From the viewpoint of the hydrologist..., it is thus usually sufficient to have longer-term averaged data of the composition of precipitation, ... which can be taken to be the input into the hydrological and ocean systems."

This said, however, YURTSEVER & GAT do note certain hydrological studies where advantage has been taken of the variability in the isotopic composition of individual rainfall events.

Although we may recognise that the examination of local and short period isotopic variations in precipitation is desirable, progress by research in this field appears to be slow, most probably because, at this scale, concern

is with individual anomalies rather than with large scale statistical averages, but indications of physical processes are too 'grouped' to allow meaningful deterministic modelling.

The patterns found in within-storm and whole-storm studies (category (3), above) may be summarised:-

(1) Initial enrichment with the onset of a storm, followed by isotopically depleted precipitation.

(2) A relationship of isotopes in precipitation with the altitude of the front above the ground surface, for frontal (notably cyclonic) rainfall, both within and between storms.

(3) A random component.

DANSGAARD's (1961) study of North Atlantic frontal rainfall over Greenland was the first to show the effect of initial isotopic enrichment. This was later found by EHHALT et al. (1963) in the contrasting situation of a convective thunderstorm over Heidelberg. In the latter case, δD_{SMOW} values fell from -10 to -30 $^{o}/_{oo}$ from the beginning to the end of the storm using an approximately hourly sampling interval. The pattern of isotopic depletion appeared to correspond to the increase in relative humidity which accompanied the fall of rain, most noticeably at the beginning of the storm; and the fairly constant δD value measured towards the end of the storm also indicated that isotopic exchange, rather than a rainout (Rayleigh-type), effect might be responsible for the observed variations (since isotopic rainout would result in increasingly isotopically depleted rainfall). Residual random variations in this particular rainfall, however, remained unexplained.

LAWRENCE et al. (1982) explore the relationships in frontal precipitation between ground air temperatures and the isotopic composition of rainfall within and between storms over the North Eastern seaboard of the

United States. The observed direct relationship between δD and (weighted average) temperature, is attributed to a correspondence of ground temperature with the altitude above the ground of the frontal surface, at least in the January storms examined. Precipitation forms just ahead of this surface, and the higher the surface the greater the relative depletion of stable isotopes in the precipitation. This effect is shown schemtically in fig. 2.21 for a warm and a (typically steeper) cold front. The situation in nature,however, is rarely simple, since individual cloud developments may introduce a random component into within-storm isotopic patterns in rainfall. The between-storm relationship of ground temperatures (and frontal elevation) to isotopic composition may equally be obscured by seasonal shift in cyclone trajectories so that changes in the isotopic evolution of the air masses dominate over any temperature relationship. LAWRENCE et al. (1982), attempted, with some success, to assess the impact of changing storm trajectories on the isotopic composition of the whole-storm precipitation. Such an approach is valuable in considerations of reconstructing palaeoclimates in terms of former patterns of atmospheric circulations.

For a maritime area such as the U.K., where a variety of distinctly different air mass types may be experienced, the synoptic scale of approach appears particularly attractive for the understanding and/or prediction of isotopic inputs, and this aspect will be explored further in this study.

2.3.3 Modification of the isotope signal in (terrestrial) hydrological systems

The previous discussions in section 2.3.2 have centred around the generation of the isotope input signal for hydrological studies and the signal's relationship with climatic, meteorological and geographical variables. Understanding and/or assessing the input signal is an important step in defining the suitability of an area or of a hydrological system for stable isotope studies. The hydrological implications of an input signal may

be such that natural tracing at a seasonal timescale, for example, may hold severely limited expectations in a particular study area. The input signal, however, must be judged in consideration of the terrestrial part of the hydrological to be studied. It is the *modification* of the input signal, in the water's progression through the terrestrial part of the hydrological cycle which conveys the greatest information to the isotope hydrologist. The processes of terrestrial modification of the input signal were included schematically in fig. 2.10.

Of most importance for hydrological studies are the processes of mixing and storage during the water's transmission through the cycle. Due to the relatively conservative properties of the stable isotopes (section 2.2.5(e)), this process may be assessed simply by the comparison of the isotopic output signal with the input signal. Normally, smoothing rather than enhancement of the isotope signal occurs. Use of the environmental isotopes in this way contributes to the assessment of a system's input-output response, and is the basis of 'natural tracing' studies.

The choice of an output sampling point in a system defines the resolution of the hydrological 'black box' in which mixing and storage may be operational. It is important to note, however, that the isotopic composition of the water in transit may be modified in three additional ways, which are dependent upon the climatic and vegetational conditions of the area as well as on its hydrological regime. The processes involved are (1) evaporation, (2) exchange with atmospheric gases, and (3) inclusion in sediments or organic materials.

Modifications of signal will be discussed only briefly here, since the theoretical arguments for their occurrence, in terms of isotopic fractionation, are adequately covered in section 2.2.5.

Examining processes (1) and (2) together, fig. 2.22 (modified from GAT & TZUR, 1967), shows schematically the occurrence of evaporation and exchange

with atmospheric water vapour in the terrestrial part of the hydrological cycle. Both processes cause isotopic fractionation. Evaporation generally produces isotopic enrichment and a lowering of slope in the $\delta^{18}O$-δD relationship of the residual water, when there is kinetic control on evaporation (section 2.2.5(d)). Exchange of oxygen isotopes with atmospheric CO_2 causes a relative depletion of ^{18}O in the water (fig. 2.4), but this effect is thought to be of minor importance for bodies of surface water in the terrestrial environment, due to the low atmospheric concentrations of CO_2 ($\sim$0.03%) and long residence times required for CO_2 exchange when a smooth and limited surface area is available for interaction (BOTTINGA & CRAIG, 1969).

Above-surface stages of the recharge process include interception by vegetation, water retention in surface depressions, puddles and lakes, and overland flow (rare) and stream flow. Where water is delayed, continued evaporation will have quantitatively more effect, and of these stages the

> "...effect of interception on the isotope balance of the system is the most difficult to assess" (GAT & TZUR, op cit., p.54).

10-20% of precipitation is typically returned to the atmosphere by this evaporation from leaves (eg. 16% of precipitation returned by corn in the growing season; WARD, 1975, p.63).

Evaporative effects on water in the aerated soil zone (direct evaporation zone of fig. 2.22) are also difficult to assess since this flux may not be quantified in the traditional evaporation tank/Pichometer measurement of evaporation, nor in the Penman method of calculation. Total evaporation may have the greatest impact on a water balance, whereas partial evaporation may produce the more noticeable isotopic impact.

Examining process (3), above, the uptake and release, of the isotopes of hydrogen and oxygen into and from inorganic sediments, with which water has contact, is thought to have negligible effects on the water, at environmental temperatures, as previously discussed in section 2.2.5(e). Seasonal and

quantitative uptake of water by plants, may cause modification of the isotope signal by selective exclusion (total or partial) or delay of particular waters in their passage through the hydrological cycle, thus modifying the isotope signal (ALLISON et al., 1984). A consideration of signal modification is important in hydrological applications of the stable isotope technique, and also contributes to the discussion of the technique's appropriateness in the UK context. The importance of mixing and storage (a further modification of the signal) in isotope hydrology will be considered in discussions of applications of the stable isotopes.

2.4 The applications of stable isotope determinations in hydrology

2.4.1 Introduction

Examination of the natural variations in stable isotopes in particular stages of the hydrological cycle provides information frequently not available using other techniques; for this reason, applications of a stable isotope technique have grown in number and diversity since the first exploratory studies using such determinations, in the early 1950's (especially EPSTEIN & MAYEDA, 1953; FRIEDMAN, 1953). In hydrology, use is made of the input signal in precipitation and the terrestrial modification of this signal. In neighbouring disciplines, use is made of the stable isotope determinations wherever interaction with water causes an isotope signal to be imprinted or stored either in another material (eg. in sediments or organic matter) or else in water temporarily excluded from participation in the hydrological cycle, for example, water locked in glaciers. Such neighbouring disciplines include geology, glaciology, and Quaternary studies. The underlying principle upon which the advantages of using the stable isotope technique depend is that the stable isotopes in water may be viewed as natural tracers of the water.

2.4.2 The wider context of stable isotopes used as natural tracers

The stable isotopes of hydrogen and oxygen may be viewed as natural tracers of water because:-

(1) They are the constituents of water and therefore travel at the same speed as that water.

(2) They are conservative, ie. interaction with the medium through which they pass is minimal under normal conditions (section 2.2.5(e)).

(3) The are not toxic.

(4) Their input is areal, the rainfall itself, and requires no artificial application.

(5) The isotopic signal of input as meteoric water, or some terrestrial modification of it, provides the trace of the water.

Figure 2.23 illustrates the type of studies carried out in isotope hydrology and its neighbouring disciplines, according to the scales of study in time and space, to show how the principle of stable isotopes as natural tracers fits in context. Information flows link the fields of study and illustrate how studies using stable isotopes as natural tracers in contemporary processes are central to the body of hydrological reseach in which stable isotope techniques are applied.

Natural tracing of current recharge processes, with which this study is concerned, may take place at the scales of the catchment or region. As an example of its inter-linkage, extrapolation of observed isotope variations

(typically on a seasonal, or short period basis), may be made to interpret:-

(a) isotope variations at a point in space over a long time period, recorded in dateable material;

and

(b) regional or global variations in isotope patterns requiring interpetation at a lower spatial resolution, for a particular instant or period.

In addition, appreciation of error bars and/or the knowledge of spatial homogeneity in (b) may be fundamental in any interpretation of (a). In moving from natural tracing to examination of palaeowaters, for example, (as in (a)), we invoke the principle of the present being the key to the past; in moving to examination of whole water bodies (as in (b)), we invoke the principle of small-scale processes being the key to large-scale patterns. The same may be said of the comparable studies of stable isotopes in microfauna, tufa, organic matter or ice cores, as is suggested in fig. 2.23.

The direct use of stable isotopes as natural tracers in current processes has been a fruitful and important area of study in isotope hydrology. A suite of successful study areas within isotope hydrology may be recognised:-

(T) Tracing of water in current hydrological processes by the comparison of input with output isotopic signals.

(S) Tracing the source and evolution of a water body by its isotopic characteristics.

(E) Evaporation and water budget studies, especially of lakes and in arid areas.

(P) Palaeoenvironmental interpretation of isotopic information from water bodies.

(G) Glaciological studies using stable isotopes, especially in terms of glacier dynamics and snow pack development.

(g) Identification of geothermal waters and geothermometry.

In addition, the altitude of recharge (A) may be of concern, invoking the altitude effect on input in the tracing of water parcels or in describing the source of whole water bodies.

It is evident that in any particular study in isotope hydrology, one or a combination of the above aspects may be examined.

Certain trends in the application of stable isotopes in hydrology may be identified, according to the problems being solved, the climatic locations of studies, the scale of studies and the utilisation of supporting information. These will be examined in the following section.

2.4.3 The examination of trends in stable isotope hydrology

The development of applications of a stable isotope technique in hydrology is well reflected in the proceedings of symposia held on a (mean) 4-yearly basis since 1963 by the International Atomic Energy Agency (IAEA); symposia held in 1963, 1966, 1970, 1974, 1978 and 1983 are reported in IAEA (1963, 1967, 1970b, 1974, 1979b, 1984) respectively. In order to assess this development, all papers in these proceedings in which stable isotopes (^{18}O,D) were used in hydrological studies - a total of 104 papers - were categorised according to the aspect studied, location of field area and the scale of study unit. Results of this analysis are presented in figs. 2.24, 2.25 and 2.26.

It is recognised that by choosing to use only the specified IAEA publications, a bias is introduced in both the countries from which work is reported and the limited subject areas which may be covered in individual symposia. It is hoped, however, that periodic maxima of publications associated with the IAEA symposia (GAT, 1981a) may be sufficiently representative to identify the most significant trends through time of studies in isotope hydrology.

In this section, specific examples will be given of how stable isotopes have been of use in hydrological studies.

2.4.3(a) Trends in climatic zone of field areas and aspects of study

In fig. 2.24, studies are grouped according to the climate of the field area (classification after STRAHLER, 1969), and each one is coded to express the major aspects of isotope hydrology under investigation, using the categories specified in section 2.4.2.

Table 2.7 gives examples of the climatic types for stations in the IAEA/WMO network, relating climatic and isotopic data to the isotopic groupings used for seasonal $\delta^{18}O$-δD input data (after DANSGAARD, 1964 , and explained in table 2.6), although excluding the 'high altitude' climatic category. Figure 2.27 reproduces STRAHLER's (1969) division of the world into climatic zones.

It is logical that certain applications will be independent of climate, notably through the occurrence of the altitude effect, and of geothermal waters. (Specific examples of the altitude effect were given in table 2.5). Both phenomena may aid identification of the source of a water body, and the altitude effect may also be used in direct tracing studies (input-output response).

The climate-dependence of other activities in stable isotope hydrology will be examined by consideration of each climatic category (or group of categories) in turn.

(a) Few studies fall in the wet, tropical and subtropical climatic categories (1,2,6). This may be due to the constancy of isotope signal, providing negligible seasonal 'tagging' of the water and therefore reducing the opportunity for natural tracing. With a plentiful water supply in such areas, also, water resource development may be of a low priority (water quality, however may be of concern, rather than water quantity), providing as yet little incentive for isotopic investigation.

(b) Arid and semi-arid areas (climates 3,4,5), in contrast, have consistently been the subject of isotope hydrological investigations. Interest has been predominantly in identifying the source of water bodies, essential to the development of water resources. An example is the study by DINCER et al. (1974b) of groundwater recharge and movement in Saudi Arabia. Examination of the limited ^{18}O and chemical (especially salinity) data revealed interconnections of major aquifers and shallow recirculation of irrigation water, the latter indicated by evaporative isotopic enrichment, in groundwaters of the alluvial aquifer of Wadi Bishah.

Where palaeowaters are identified or water balances quantified using the stable isotope technique, more detailed estimations of current recharge rates are possible, hence better resource management, in terms of recommending realistic maximum extraction rates. SONNTAG et al. (1979) contributed in this way by studies in carbon-14-dated Sahara groundwaters. Groundwaters older than 20,000 years were common, and were characterised by a low stable isotope d-excess parameter, which was attributed to a lower moisture deficit of air over the ocean during the last glaciation. Modern recharge was identified in the Sahel region, by its high D and ^{18}O concentrations, probably of summer rainfall derived from evapotranspiration, and bore important information

concerning current extraction practices. In Botswana, DINCER et al. (1979) were able to assess the balance of evaporation and evapotranspiration in the Okavango Swamp, using the stable isotope technique, exemplifying its contribution to water resource evaluation in a critical area.

There has been consistent interest also in the arid zones in the natural tracing of contemporary recharge, eg. in identifying the degree of evaporative enrichment in the profile of the unsaturated zone (ALLISON et al., 1984), since such effects strongly influence the interpretations made regarding the origins of water bodies.

(c) Maritime west coast climates (climatic category 7), have received moderate attention in isotope hydrology, but the activity since 1963 is disproportionate with the concentration of isotope hydrologists and pressure on water resources (with high per capita usage) in these areas, into which category falls the U.K. Possible reasons for this might be the lack of a strongly seasonal isotopic input signal for tracing studies and for identification of, for example, evaporated surface waters. These and other factors have been explored in more detail for the U.K. situation in section 1.1.

Natural tracing studies reported (in IAEA publications) for climatic zone 7, prior to initiation of this project, were limited to studies by MOOK (1970) and MOOK et al. (1974) in the Netherlands, and by CONRAD et al. (1979) in France (the latter discussed in section 1.4.3). The exploratory study by MOOK (1970) examined the stable isotope distribution in surface, ocean, impounded estuary (the IJesselmeer) and groundwaters. Monthly sampling of the rivers Rhine and Vecht revealed their seasonal patterns in $\delta^{18}O$ to be 180° out of phase. This was attributed to the Rhine carrying isotopically light meltwater from its snow-capped source areas in the Alps, Vosges and

Jura mountains during the summer months, whilst the Vecht was fed by isotopically heavier rainfall during the corresponding period. Isotopic evaporation effects in the IJesselmeer were negligible. MOOK et al.(1974) looked in more detail at the potential of natural $\delta^{18}O$ variations as a tool in the separation of the unit hydrograph into direct runoff and baseflow components. The Hupsel Brook catchment, area 650 ha, was chosen for study, since it displayed a fast response to storm rainfall, due to the presence of only a shallow (2 m) phreatic aquifer underlain by impervious clay. Rainfall and streamflow were sampled at 8 hour intervals, and for a particular storm, with $\delta^{18}O$ input distinctly different from the baseflow value, it was computed that 87% of rainfall infiltrated into the soil (as aquifer recharge), and the remaining 13% drained out of the catchment within a few days. This illustrates a successful usage of short period variations in a fast-response system.

In the absence before 1980 of detailed stable isotope studies in the maritime mid-latitude zone of altitude effects, evaporation, recharge and aquifer behaviour, identification of source waters using this technique has been extremely limited; any interpretation of palaeowaters has also been problematic.

In North West Europe, for example, the chronology and palaeoenvironmental reconstruction of the Devensian and Flandrian epochs (ie. since 70 ka BP) of the Quaternary period are well advanced using conventional methods. Difficulties have been encountered in the U.K., however, in matching palaeoenvironmental scenarios with stable isotope evidence from groundwaters. Groundwaters dated using carbon-14 have undergone stable isotope analyses, eg. by D.B. SMITH et al. (1976), DOWNING et al. (1977) and BATH et al. (1979), in the Chalk of the London Basin, in the Lincolnshire Limestone and in the Triassic Bunter Sandstone respectively. Evaporative conditions in the Devensian have been inferred to be similar to those of the

present day from the agreement of $\delta^{18}O$-δD regression lines of old groundwaters and modern precipitation. A range of $\delta^{18}O_{SMOW}$ in groundwater has been found, in the London Basin, from -7.1 $^{o}/oo$ at outcrop (modern recharge) to -7.9 $^{o}/oo$ at the centre of the aquifer (25000 yrs. BP) (D.B. SMITH et al., 1976)). From correlations of $\delta^{18}O$ in precipitation with mean air temperatures for 5 north-west European stations EVANS et al. (1979) inferred temperatures at the time of recharge of the dated water. These were compared with a composite temperature curve for the late Devensian and Flandrian, derived from more conventional evidence. To explain the apparently higher temperatures given by the isotope technique relative to the other methods, in the late Devensian (30-10 ka BP), the following palaeohydrological interpretation was suggested: infiltration occurred of snowmelt during spring and of rainfall during autumn, with evaporation minimising summer recharge, and frozen ground preventing recharge during winter. Problems remain in matching the stable isotope data satisfactorily with other data, however, due to: (1) possible changes in atmospheric circulation patterns, (2) the mixing of waters of different ages, and (3) the problems of quantifying the effect of frozen ground. Specific stable isotope studies of varying input with atmospheric circulation and of recharge in a contemporary tundra environment would greatly assist such palaeoenvironmental studies in the mid-latitude regions.

(d) Isotope data in Mediterranean climates (category 8, fig. 2.24) have provided information principally concerning water source. STAHL et al. (1974), for example, identified three altitudinal 'isotopic provinces' of artesian springs and found a varying mixture of brackish and fresh waters in geothermal springs in the Sperkhios Valley in Greece. Certain studies have also attempted to use the seasonal input component in this area for tracing studies. GAT (1974) found the isotopic scatter of $\delta^{18}O$ values in

precipitation to be retained but reduced in repeated sampling of waters from the karstic aquifer of the Judean Mountains, but water was found to be practically homogenised in a sandstone aquifer in Israel's coastal plain.

(e) Mid-latitude desert and steppe zones (climate 9) have been relatively neglected. Perhaps further pressure on agricultural land in these areas (the principal wheat-growing regions) will provide an incentive to explore further water resource development here, where a clear isotopic signal (high σ^2 in input, table 2.7, DANSGAARD type III) is available for tracing purposes. In certain areas, the distinction between this, and the more intensively studied climatic category 10 is not clear.

(f) The activity of isotope hydrologists in the continental climates (category 10) has been prolific, and has diversified with time. A clearly seasonal isotopic input (type III, table 2.6) is provided, and advantage of this has been taken, paticularly in tracing recharge water in soil profiles. An example is the isotopically depleted snowmelt providing a marker in recharge through Swedish sandy soils (SAXENA & DRESSIE, 1984). A range in $\delta^{18}O_{SMOW}$ from -15 to -11.5 °/oo in the measured soil moisture profiles was compared with the range in (weighted, monthly) precipitation of -18 to -8 °/oo. Annual downward displacement of recharging water was found to be ∿160 cm/yr. using this method.

Short period studies have also been carried out in this climate. RODHE (1984), for example, exploited isotopic signals in snowmelt and in individual rainfall events, for hydrograph separation, from daily sampling of waters, in 10 small Swedish catchments, each of which had a shallow groundwater table in till soil, above a granite/gneiss bedrock.

A variety of water source investigations have been carried out in this climatic zone, for example, RODRIGUEZ (1979) in Colombia and BORELI et al.

(1979) in Yugoslavia. It is apparent, however, that in most cases, information additional to the stable isotope data contributes very significantly to the final interpretation.

(g) Few studies of stable isotope hydrology in areas of high latitude (climatic categories 11-14) have been reported in IAEA proceedings, despite these being the areas for which DANSGAARD (1964) first considered the use of stable isotopes. Numerous studies of palaeoclimate, using isotope data from ice cores, and investigations of glacier dynamics using stable isotopes have, however, been presented elsewhere, and are reviewed by ROBIN (1983) and ARNASON (1981).

Significant contributions could be made in the future by studies of isotope hydrology in the subarctic and tundra zones (climates 11-13), to assist in interpretations of (periglacial) palaeohydrology in lower latitudes, as noted previously for the U.K.

(h) Studies carried out in high altitude climatic zones (category 'H') have predominantly made use of the natural tracing properties of the stable isotopes. Such areas are normally associated with high available relief, within a small area. This has the effect of reducing the opportunity for water mixing and storage. A faster throughput rate may result and the isotopic signal in precipitation may be less likely to be lost in natural tracing.

The following additional advantages are found in high altitude areas, for isotopic studies using stable isotopes: (1) the 'altitude effect' in precipitation may be used to determine the mean altitude of recharge of particular waters (examples were given in table 2.5), and (2) seasonal input of snowmelt from a higher to a lower altitude may provide an enhanced tracer

'tag', as used, for example by DINCER et al. (1970) in Czechoslovakia, and by SKLASH et al. (1976) in the Canadian Rockies. The latter is a non-IAEA publication and reports a method of hydrograph separation, using oxygen-18 as a natural tracer. In addition, (3), many of the high altitude areas also receive the strongly seasonal isotopic signal of a surrounding continental region. It is only the inaccessibility, or else the lack of incentive for water resources development, which limits the use of the stable isotope technique in such areas.

2.4.3(b) Trends in the scale of investigations in isotope hydrology

Figure 2.25 illustrates, for IAEA symposia proceedings, the number of papers reporting studies in each of four categories of scale, viz. the units of country, region, hydrological basin and point/profile studies. These are rather arbitrary units, especially in the category of the 'region' which has no physical or political expression. This unit may be distinguished from the 'country' by the latter's implication of a choice of scale appropriate to comparisons of isotopic patterns across the globe. Both of the above units tend to cross hydrological basin boundaries.

The linkages between scales of study and the aspects of isotope hydrology under consideration were shown in fig. 2.23. The use of the country as a unit (fig. 2.25) has declined since 1974, as the initial studies of worldwide isotope patterns are replaced by more specific studies of physical processes, rather than their spatially averaged statistical expression. The continuing growth of regional unit applications, however, reflects the utility of the stable isotope technique as an exploratory tool, especially in terms of the identification of the source of water in an aquifer (eg. by DINÇER et al.,1974b , in Saudi Arabia).

The interesting upwards trend of studies concentrating at the smaller scale - the basin and point/profile studies - is typical of many other branches of the environmental sciences. The studies are normally associated

with a higher temporal resolution and aim to explain more of the observed variation of natural phenomena by examination of the fundamental physical processes concerned. Increasingly at this level, the testing of hypotheses takes place by controlled experiments. An example is the use by FÖRSTEL (1984) of a soil lysimeter in a climate chamber, to investigate recharge mechanisms and isotopic modification due to moisture uptake by plants.

2.4.3(c) Trends in the use of combinations of environmental isotopes in hydrological studies

Figure 2.26 plots, for IAEA symposia proceedings, the breakdown of papers incorporating stable isotope studies, according to the combination of environmental isotopes used (from $\delta^{18}O$, δD, ^{3}H, $\delta^{13}C$ and ^{14}C). Initial enthusiasm for the use of stable isotopes as hydrological indicators which could be used in isolation (in exploratory work of the 1960's) was soon tempered by the need for supporting data. Environmental isotopes in combination are viewed as a powerful tool, since each isotope may be used to provide specific information about the water under investigation (age, origin, interaction with host rock, etc.).

Three points may be noted from fig. 2.26:-

(1) In the use of stable isotope species in isolation, $\delta^{18}O$ has been more popular than δD, but only in 1974 did single $\delta^{18}O$ analyses outnumber studies using $\delta^{18}O$ and δD in combination.

(2) The number of combinations of environmental isotopes has expanded through time, the multi-analysis approach now dominating isotope hydrology. One might suggest that were the field of absolute groundwater 'dating' (using ^{14}C and other radioactive isotopes) not so problematic, this factor might not be so noticeable today.

(3) Although the utility of tritium as a dating technique has reduced with the low levels now found in precipitation and with the decay of the bomb tritium peak (section 3.3.1(b)), this isotope continues to be included in multi-analysis studies.

It may be noted that in large, sensitive projects, such as the Stripa project of hydrological investigations for nuclear waste disposal (MICHELOT et al., 1984), every environmental isotope technique available is used, in the hope that more precise identification of the hydrological systems will result. If the same approach is to be applied in the U.K., it is important that systematic process studies are previously undertaken, in order to fully understand the contribution of stable isotope analyses to such projects.

PART 3 STUDY AREAS AND METHOD

3.1 Introduction: research design

In Part 3 of this study, the research design is presented in terms of the choice of study areas and sampling programme. Physical features of the areas and sampling locations are discussed (in section 3.2). Field sampling and analytical (laboratory) procedures follow in sections 3.3 and 3.4 respectively. Finally, in section 3.5, methods in which significant experimental work was undertaken in this study are presented. Results from these experiments provide recommendations for future studies in which stable isotopes are to be used as natural tracers.

3.1.1 Choice of study areas

It was considered essential in this study to choose field areas which were hydrologically 'well-known', that is having been the subjects of previous studies, using conventional hydrological methods. Documentation of the behaviour of such systems could thus be used to provide essential background data for the interpretation of the stable isotope measurements. In this way, the new technique was to be validated for use in the U.K.

To investigate the magnitude and timing of the response of surface and groundwaters to the isotopic input signal, areas were chosen with hydrological regimes near the extreme ends of a theoretical spectrum of regimes where the rate of transmission of rainfall through the aquifer is the key criterion, as previously discussed in Part 1.

The study areas chosen were:-

1. The Malham area, North Yorkshire; an area of horizontally-bedded and strongly karstified Carboniferous limestone, in which conduit

flow is thought to dominate. In addition, an adequate altitudinal range is found here (472 m) for investigation of the isotopic altitude effect.

2. The Lambourn area, Berkshire; an area of Cretaceous chalk in which diffuse-type flow is thought to dominate.

Section 3.2 provides descriptions of the study areas with respect to their geology, landforms and soils, climate and drainage. Figure 3.1 shows the locations of the two areas in the U.K.

3.1.2 Choice of sampling programme

A systematic sampling programme in terms of sampling locations and the frequency of sampling, was designed in accordance with the objectives (1) to (6) of the study which were specified earlier (section 1.2). The major features of the programme are presented in table 3.1. Precipitation, surface waters, groundwaters and intermediate waters in the hydrological cycle (cave drips and soil waters) were all to be sampled. Groundwaters are defined, for the purpose of this study, as waters which are extracted from the ground via boreholes, whilst surface waters are sampled directly at the earth's surface. The examination of precipitation was considered to be of particular importance in the research design since the strength of the isotopic signal contained therein would determine to a large extent the potential of the stable isotope technique for natural tracing. The monthly sampling programme provides a background to more detailed investigations of both precipitation and surface waters.

3.2 Study areas and sampling locations

3.2.1 The Malham area, North Yorkshire

Figure 3.1 shows the location of the Malham study area in North Yorkshire. This upland area consists of predominantly karstified Carboniferous limestone. Hydrological observations and experiments have been

well documented in this region since the 18th century, as shown by HALLIWELL (1974).

The area under consideration is that included between Capon Hall in the west and Great Close Hill in the east, and between Airehead Springs, 650 m south of Malham village, in the south, and Fountains Fell in the north, as shown in fig. 3.2. Its area is approximately 15.5 km^2 and its altitudinal range from 185 to 657 m O.D. over a horizontal distance of 8.5 km. The area forms the upper watershed of the River Aire. The contributing waters of Gordale Beck to the east, and of Tranlands Beck draining Pikedaw and Kirkby Fell to the west are, however, omitted for the purposes of this investigation. Drainage northward from Tennant Gill towards Cowside Beck (Skirfare) and the River Wharfe is also excluded. It is admitted that a true catchment in an area of karst, where drainage networks may bear little relation to surface morphology, is difficult to define. A requirement of this study, however, was to monitor variations of stable isotopes in the different stages through the terrestrial part of the hydrological cycle, rather than to establish a water budget for the whole area.

In this section, details of the area's geology, landforms and soils, climate and drainage will be given as background to the choice of sampling sites, which are described in section 3.2.1(e).

3.2.1(a) Geology

A detailed account of the geology around Malham is well presented by O'CONNOR (1964) (revised in SHAW, 1982), while GARWOOD & GOODYEAR (1924) provide the standard reference for the important Lower Carboniferous succession. WRAY (1936) gives a useful overview of the regional geology, and WALTHAM (1974) is recommended for a more modern review of the limestone geology in this locality. The most important features of the area's

geological structure and lithology will be outlined here and their hydrological implications examined.

The Malham area lies at the southern margin of the stable Askrigg structural block which, together with the Alston Block, underlies the northern Pennines. The Mid- and North Craven Faults cross the study area (fig. 3.3); the Mid-Craven Fault was already active in the Lower Carboniferous period, forming a prominent scarp with a downthrow of approximately 120 m to the south, according to HUDSON (1944). The present scar of Malham Cove (plate 1) appears to be the result of erosional retreat from the Mid-Craven Fault. WAGER (1931) considers the large North Craven Fault to have been produced in the Variscan orogeny, which followed the Carboniferous period (c. 270 m.a. B.P.), probably forming along an ancient line of weakness. Erosion along the North Craven Fault has exposed the inlier of Silurian rocks north of the Fault, beneath the present Malham Tarn. Exposures in the remainder of the area are of Carboniferous and more recent deposits.

Figure 3.4 shows diagramatically the correlation between the lithological sequences north and south of the Mid-Craven Fault. The characteristics of the strata will each be described briefly, in order of age.

It is assumed that the Carboniferous limestones in the area are underlain by the Ingletonian series of siliceous slates (HALLIWELL, 1979). Investigation of the characteristic negative gravity anomaly in the region by DUNHAM (1974) revealed a granite batholith, yielding a Rb:Sr age of 400 million years, which may be taken as the minimum age for the surrounding slates. The inlier of metamorphosed Silurian slates is mostly drift-covered, but the proximity of the lower Palaeozoic floor is indicated by the line of springs which mark the junction between the well-jointed Great Scar Limestone and the impervious slates.

The slates form an uneven topography upon which has been deposited, to the North of the Mid-Craven Fault, the Great Scar Limestone. This is a

rhythmic succession of very pure, fine-grained, bioclastic limestones, varying from 100 to over 200 m thick, and is very well exposed in this area. The insoluble residue of the limestone is found in chemical analyses presented by WALTHAM (1974) to average approximately 2% by weight. The primary porosity of the limestone is low and the rock virtually impervious to water, as noted by SWEETING & SWEETING (1969). Drainage, and thus the solution process, is restricted to joints and bedding planes. Bedding is particularly well developed in the upper (D_1) limestones, and O'CONNOR (1964) has measured a regional dip of approximately 5° to the north-west. Vertical jointing cuts through the bedding plane and commonly two sets of joints are developed at right angles, the conjugate joints referred to by DOUGHTY (1968). These are most common between the Mid- and North Craven Faults, trending NNW-SSE, and ENE-WSW (WAGER, 1931). South of the Mid-Craven Fault during the Lower Carboniferous times, limestones similar to the Great Scar series formed, but differed in the development of dolomitic and reef limestones (see O'CONNOR, 1964, for a discussion).

The Yoredale series formed in the Upper Carboniferous period and lie above the Great Scar Limestone, north of the Mid-Craven Fault. They form a rhythmic series which may be divided into cyclothems, consisting of coal, sandstone, shale and limestone. They cause drainage to move off sandstone, over shale and into limestone at the base of each cyclothem (HALLIWELL, 1979). The net effect of the largely impermeable Yoredale strata is to transmit precipitation to the contact with Great Scar Limestone, where drainage continues underground, as marked to the south and east of Fountains and Knowe Fell by a high density of enclosed depressions. In the east of the area, most of the Yoredales have been eroded off, although about 1.5 m of sandstone is found at Parson's Pulpit. Between the North and Mid-Craven faults, sandstone is absent in the Yoredale series and there is an 'overlap' of the Bowland Series of shales (HUDSON, 1944), which are found south of the Mid-Craven Fault

and are closely jointed and thus effectively impermeable. Millstone Grit caps the areas of relatively high altitude to the south of the Mid-Craven Fault (Kirkby Fell), and to the north (Fountains Fell).

The detailed topography of the area has been much influenced by glacial action in the Pleistocene, together with the deposition of glacial and periglacial drift deposits. These sediments all appear to be of local origin, which suggested to RAISTRICK (1926) the former existence of a local ice cap. The drifts are of variable thickness and extent, large amounts having been removed since Late Glacial times, c. 10,000 yrs. B.P. (O'CONNOR, 1964). Analyses by BULLOCK (1971) suggest the loamy deposit found on limestones, and often in conjunction with a thin band of plastic clay, to be an aeolian deposit, ie. loess. This underlies the Tarn and Tarn Moss. Solifluction deposits of sandstone, grit and clay coat the middle and lower slopes of Darnbrook and Fountains Fell, and these probably rest on high level till of the same materials (O'CONNOR, 1964), derived from the Yoredale beds. South of the Tarn, fluvioglacial gravels and sands occur, and a full account of these features may be found in CLARK (1967).

3.2.1(b) Landforms and soils

Geomorphologically, the study area may be divided into four categories, which coincide in part with the major divisions of BULLOCK (1971) for soils:-

1. Fells of the Yoredale series, capped by Millstone Grit
2. Drift-covered hummocky ground
3. Great Scar Limestone plateau
4. Airedale lowlands

The main features of each category will be presented, but for a more full discussion of the Malham area in particular the reader is referred to CLAYTON (1981), and for setting in the context of North West Yorkshire, to SWEETING (1974, pp.46-73).

(1) The fellsides of the Yoredale series, rising to 657 m on Fountains Fell reflect the cyclic pattern of lithologies, producing a stepped cross-section. Peats and podsols are found on the resistant Millstone Grit capping. The degree of podsolisation and gleying downslope is largely dependent upon the local occurrence of tills, although drainage is generally most impeded over the shales, and elsewhere brown earths are common. Plate II illustrates a typical peaty podsol on Turf Hill.

(2) Hummocky ground is found in association with glacial meltwater and periglacial features on the plateau area and lower hillslopes. With impeded drainage, peaty gleys and peaty gleyed podsols are commonly found here (BULLOCK, 1971). The areas of enclosed depressions over the Great Scar Limestone have previously been noted (section 3.2.1(a)), and their development, in which the presence of drift is an important factor, has been studied by CLAYTON (1966).

(3) The Great Scar Limestone plateau, at average altitude 388 m O.D. (MANLEY, 1957), characteristically has thin soils, mostly organic rendzinas. Where soil cover has been lost or else never developed, limestone pavements are exposed, with solutionally enlarged joints. Crags are common, especially where dry valleys have been cut, the origins of the latter being discussed by CLARK (1967).

(4) The lowlands, at average altitude 185 m O.D. constitute a relatively minor proportion of the study area (5 %). Gently rolling topography is found in the wide valley head of the River Aire, with impeded drainage where the Bowland Shales outcrop.

Table 3.2 gives an assessment of the relative areas of land use in the study catchment.

3.2.1(c) Climate

MANLEY (1957) describes the uplands around Malham Tarn as windy, humid and cloudy, many days having measurable rainfall. Records of rainfall have been kept at Malham Tarn House (now Malham Tarn Field Centre) since 1870 (JONES, 1981), and in 1948 climatological observations were commenced as a third-order station. The altitudinal range in the study area (185 to 657 m) and the topographic influence on local climates, however, makes a representative assessment of climatic conditions over the catchment rather problematic.

At Malham Tarn, mean annual precipitation for the period 1881-1915 (SHAW, 1957) was 1473 mm, this amount falling on average in 220 days. There is a large excess of precipitation over evaporation, effective precipitation forming, for example, 74 % of total precipitation in 1980-82. Monthly precipitation amounts are recorded for Fountains Fell, and are generally higher than those reported at Malham Tarn Field Centre, the annual average precipitation on the fell being 2000 mm (BULLOCK, 1971). SMITH (1972), however, notes a considerable scatter in the relationship between elevation and mean annual precipitation, which may be important in considerations of the stable isotope input over an area of considerable altitudinal range. The characteristic rainfall systems of the area are of unstable polar-maritime air from the north-west, which may be deflected by topography, and of heavy and persistent orographic rainfalls, both of which tend to produce an increase of rainfall with altitude. Reversals of this effect, however, may occur. A case is reported, for example, by CHAPLAIN (1982) where severe storms in June 1982 over West Yorkshire caused hill stations to record monthly rainfall totals significantly less than lowland stations in that region.

Snowfall is expected at Malham Tarn on 47 days per year, and snow to be lying on 40 days. This compares with observations of snow lying on Fountains Fell summit for 80-85 days in the year (MANLEY, 1979). The average annual air

temperature at Malham Tarn (1921-1950) is 7.0°C. Temperature lapse rates, significant in calculations of isotope variations with altitude, have been considered in detail by MANLEY (1957, 1979). Upland areas of the Great Scar Limestone plateau and above have lower daytime maxima, the decrease with height tending towards the dry adiabatic lapse rate of 0.91°C/100 m. Daily minimum temperatures in the uplands, however, are similar to those in the lowlands, and temperature inversions frequently occur. MANLEY found, for mean daily temperatures, an average lapse rate of 0.56°C/100 m from Giggleswick, at 175 m O.D., 10 km WSW of Malham Tarn, to the Tarn House. From the latter to Fountains Fell, he found an average lapse rate of 0.81°C/100 m. He attributed the deviations from the anticipated lapse rate of 0.65°C/100 m, for northern Britain, to the local amelioration of climate as measured on the lawn in front of Malham Tarn House. The southerly aspect, sheltering from the wind by the scar to the north and proximity to the Tarn water body were all suggested as contributing factors. MANLEY (1979) anticipated a lapse rate of approximately 0.68°C/100 m from the limestone plateau to Fountains Fell summit, were the effects of local amelioration of climate at Malham Tarn eliminated.

3.2.1(d) Drainage

The drainage in the Malham area may be viewed as a cascading system, as shown in fig. 3.5; it results from litholigical controls which have already been considered in a discussion of the area's geology. It is convenient to discuss separately the parts of the system which lie north and south of the North Craven fault. Much work has been carried out on the transmission of water through Great Scar Limestone, after it crosses the North Craven fault, and this is examined after consideration of the upper part of the Malham area, which has been less well documented.

Drainage north of the North Craven fault

Rain falling on the upland fells is seen to be transmitted principally to sink holes, either into the limestone of the Yoredale series at higher

altitude, for example on Knowe Fell at 510 m, or into the Great Scar Limestone, for example on Chapel Fell at 450 m (figs. 3.2, 3.5). Transmission by throughflow in this area occurs by slow drainage through the peat, more rapidly through the more permeable layers in podsols or at the soil base, and perhaps most rapidly through soil pipes (JONES, 1971). Only a few sinking streams exist, and of these only that terminating at NGR SD 870688 on Knowe Fell is perenially flowing.

Water passing through the Great Scar Limestone is thrown up at the junction with impermeable Silurian slates, as noted in section 3.2.1(a). In the study area, such springs form the sources of the Smelt Mill sinking stream and the feeders to Malham Tarn. To the south and east of Great Close Hill (NGR SD 902668), contact springs also form the sources of Gordale Beck.

Malham Tarn itself (plate III) covers approximately 62 hectares; it has a maximum recorded depth of 4 m, while most of the offshore parts are between 2 and 3 m deep (HOLMES, 1965). Springs rise up through the floor of the Tarn (GLOVER et al., 1977), which is coated with an almost pure deposit of calcium carbonate, about 15 cm thick. Springs also emerge in 'peat pools' to the west, in the Tarn Moss area. The main feeders to the Tarn originate however, from springs near Waterhouses (NGR SD 887673) to the north-west and towards Capon Hall (NGR SD 877668) and Higher Tren House (NGR SD 883667) to the west. Smaller volumes feed from springs at the foot of Great Close Hill to the east of the Tarn. Outflow from the Tarn is to the south down an artificial slipway which, with the optional use of sluice gates, controls the level of the Tarn. The outflow cuts through kame deposits and passes over impermeable glacial drift, until it sinks into the Great Scar Limestone, south of the North Craven fault.

Drainage south of the North Craven fault

The majority of interest in the area south of the North Craven fault has been directed at the passage of water through the underground 'black box' of

the Great Scar Limestone, and in particular the linking of sinks with emergent streams. It is to be noted that rain falling on this area adds to the volume of water being transmitted through the 'cascade'. The majority falls on thinly covered limestone, being directly transmitted to the aquifer. Additionally, rain falling in the west on the Yoredales of Black Hill and Haw Knabs will experience conditions similar to those described north of the North Craven fault. It is possible that water from this area is transmitted east into the study area, as suggested by a positive water trace from Gorbeck Cave (NGR SD 865658) to Malham Cove springs, reported by GALLIVAN (1980).

There are two major sinking streams of interest in this area. The first is the outflow from Malham Tarn, which normally sinks into the Great Scar Limestone at Water Sinks (NGR SD 894655), 700 m south of the Tarn. The second sink occurs at Smelt Mill or 'Streets' (NGR SD 882660), where a smaller stream flows across the Silurian slates, before sinking into the Great Scar Limestone. There are equally two major springs emerging near the base of the Great Scar Limestone. First are the springs at the foot of Malham Cove (NGR SD 898642) which form the Malham Beck. The Beck flows first across Great Scar Limestone, crossing the Mid-Craven fault onto 'reef' limestones and southward over the Bowland Shales through Malham village. Second, are the Airehead springs (NGR SD 901622, plate IV) which lie on the southern limb of the syncline where the shales overlie the limestones, 650 m south of Malham village. The Airehead water joins Malham Beck to become the River Aire.

The earliest report of interest in underground flows in the Malham area dates from 1751 (in HALLIWELL, 1974), when R. Pococke noted that water at Malham Tarn was locally believed to re-emerge at the Airehead springs. TATE (1879) reports the inference by inhabitants of Malham that the Cove springs were fed by Smelt Mill sinks, due to their turbidity from peat waters. However, conflicting descriptions were found and experiments were initiated by the Yorkshire Geological and Polytechnic Society to investigate the

underground flows. TATE found links from the Tarn Outflow to both Malham Cove and to Airehead by the transmission of a pulse wave from the Tarn sluices. To explain the earlier arrival of the kinematic wave at the most distant spring (Airehead) particular subterranean passage morphologies were suggested.

It was considered unlikely, however, that the Smelt Mill sink fed Malham Cove springs (or Airehead), due to the very high water hardness and small discharge, which did not correspond with the springs. After an unsuccessful attempt at tracing by THOMPSON (1891), the problems were redefined by HOWARTH et al. (1900), who proceeded with further experiments in the area. The results are summarised in Table 3.3. Attention is brought to the fast responses of the systems to both pulse waves and chemical tracers. Included in the table are results from SMITH & ATKINSON (1977), who have performed the most recent systematic investigations into underground flows in the Malham area.

The results obtained in experiments by HOWARTH et al. (1900) and by SMITH & ATKINSON (1977) were qualitatively similar. In both cases, pulse methods established a clear link from Water Sinks to Airehead springs with an irregular response at Malham Cove. Chemical tracers from Water Sinks established a strong connection to Airehead springs and a weaker connection to Malham Cove. SMITH & ATKINSON (1977), using Pyranine and Lycopodium spores, additionally traced water from Smelt Mill to both lower resurgences.

Interpretation of the data obtained differed, however, in the two major studies. HOWARTH et al. (1900) attempted to explain the course of the sinking Tarn water in terms of the development of the Watlowes dry valley, which runs to the top of Malham Cove, and to which the valley containing the Water Sinks appears to contribute. A waterfall flowed down this valley and over Malham Cove after severe storms, until the early nineteenth century (HALLIWELL, 1979). After this time certain occurrences are noted of water flowing higher in the valley, over Comb Scar, but with increasing rarity (HOWARTH et al.,

1900). A model was proposed by HOWARTH and co-workers of the stream from Malham Tarn receding up the Watlowes since periglacial times, allowing for a continued underground link to Malham Cove. Master joints were then supposed to have captured the main flow and a path developed to Grey Gill (at NGR SD 908638, with flow parallel to the master joint pathway of Smelt Mill water to Malham Cove; see fig. 3.2), from where orthogonal jointing led, in theory, to Airehead. This idea avoided the underground crossing of the linked streams, but unfortunately, no connections were established with water in Grey Gill Hole, a cave described by BROOK et al. (1976). P.F. Kendall, in an appendix to HOWARTH et al. (1900) added the concept of flow occurring in two parallel, underground valleys, to allow for 'overspill' to Malham Cove in lower discharge conditions, and rejecting the possibility of flow in conduits. An alternative model for the transmission of flow from Water Sinks to Airehead and Malham Cove was proposed by SMITH & ATKINSON (1977), after quantitative analysis of the tracing and pulse wave data, and in view of studies reported from other limestone areas. In this model, water from major sinks may feed both major springs but the main water-carrying conduits cross underground.

An important feature of the model is a restricted (boulder-choked) connection to Malham Cove of water derived from the Tarn, whilst flooded conduits beneath the Bowland Shales allow rapid transmission of this water to Airehead. This feature is included in the lower part of the 'hydrological cascade' (fig. 3.5).

Exploration work by the Cave Diving Group has shown that the Cove spring issues from an underwater passage, initially inclined at 45° and then near horizontal along a bedding plane to a distance of 50 m, where strong currents were detected, but where boulders prevented further penetration (CAVE DIVING GROUP, 1970, 1976). Diving at the Cove has more recently concentrated at the Flood Rising, slightly to the east of the permanent flow. This rising is similar in its characteristics, and has been explored some 150 m (CAVE DIVING

GROUP, 1977, 1979). Attempts to dig down from Water Sinks revealed a shaft and a boulder-choked chamber, which have since been filled in (BROOK et al., 1976).

In the absence of further major and penetrable caves in the Malham area, our understanding of the underground mixing and storage processes in the hydrological cascade is dependent upon our ability to interpet characteristics of the output waters with respect to the input of the 'black box'.

3.2.1(e) Sampling locations

Figure 3.3 shows the locations of sites where sampling of surface and groundwaters took place in the Malham area. The full sampling period extended from (the beginning of) November 1980 to February 1983.

All the sites were permanently flowing, except where indicated in the text. For each location, details will be given of:-

1. Abbreviation (in brackets after the full name), used for reference, and in certain cases marked on fig. 3.3; National Grid Reference (NGR); altitude above Ordnance Datum.
2. Hydrological background details, apart from those already discussed in consideration of drainage of the area.
3. The proximity of the sampling point to the sink/spring, where appropriate.
4. Any severe limitations on the period of sampling.

In order to investigate the intermediate stages in the transmission of rainfall to ground or surface water, samples were taken of soil water and of cave drips, and the sites chosen are included in this section. Additionally, brief details are given of sampling locations for precipitation in the Malham area, which are also marked in fig. 3.3.

Surface and groundwaters

Knowe Fell sinking stream (KFS) (NGR SD 871687; altitude 510 m O.D.)

This is the most southerly of a group of sinking streams to the north of Knowe Fell, and the location of which was verified with the use of aerial photographs. The other stream channels in the group are dry for most of the year. KFS appears to be fed by a pipe which captures flow from a Yoredale limestone stratum. A proportion of this water is abstracted at source from a settling trough (NGR SD 870687), feeding a small reservoir downslope (NGR SD 876687), which is known to supply the Malham Tarn Field Centre. BROOK et al. (1976) report an excavation of the stream's sink, named W.R.P.C. 3 (entrance now collapsed), by the White Rose Potholing Club, who found an 8 m drop to a chamber with several short outlet passages. Sampling of the stream water in this study took place within 2 m of the stream sink, although discharge was measured more conveniently 5 m upstream. Access to the site was difficult in periods of hill fog or snow, and occasionally several attempts had to be made. The period of sampling was limited from May 1981 to October 1982.

Waterhouses spring (WH) (NGR SD 887673; altitude 375 m O.D.)

This is one of the main feeders to the Tarn. HOWARTH et al. (1900) imagined most of the water sinking on Knowe Fell to re-emerge here. TERNAN (1971), however, suggests that the system is fed by percolation waters, probably from the High Mark area; he concluded this because of the low degree of dissolved calcium carbonate variation and temperature variations which he observed (with coefficients of variation of only 5.84% and 1.63% respectively). The measurements, however were only taken over a four-month winter period. Large quantities of quartzitic sand are thrown out by the spring in periods of high flow, and these could originate in either of the suggested source areas.

A dry valley, the route of the Pennine Way, runs north above Waterhouses, although slightly offset to the east from the major spring noted. This is the West End channel described by CLARK (1967) and shown to carry exceptional winter flood water in a report by DISNEY (1975, his plate III). The valley's relationship with underground hydrological pathways, however is not known.

Sampling took place either in the large spring pool, or 40 m downstream at the rectangular weir (plates V and VI), installed in July 1981, details of which are given in section 3.3.2(a).

West Great Close spring (WGC) (NGR SD 898670; altitude 375 m O.D.)

This spring is the more northerly of two small springs which emerge in an area which appears to have been quarried, and which unite after a short distance to flow down an artificially lined channel into Malham Tarn. A bed of fine quartz sand is found in the spring pool. Measurements by TERNAN (1971) showed the two springs to be chemically similar, both having low coefficients of variance (2.18%) for calcium hardness, which, on the schema of SHUSTER & WHITE (1971) indicates a diffuse-type source. GLOVER et al. (1977), noting the slow response of these springs to rainfall, suggest that they are essentially fed by local percolation water from thinly vegetated limestones and their associated pavements.

Sampling took place at WGC from January 1981 to October 1982. Two additional 'contact' springs, similar in behaviour to WGC, were sampled less frequently. The first is a 'peat pool' in the Horseshoe Wood of Tarn Moss (fig. 3.2) (NGR SD 884672; altitude 375 m O.D.) approximately 35 m SW of Waterhouses spring. The pool was sampled only from February to July 1981, after which visits to this ecologically delicate site were discontinued, in view of the general similarity of response of the spring pool to that of WGC. The second spring was at Great Close Scar (GCS) (NGR SD 900667; altitude 385 m O.D.) approximately 30 m SE of WGC spring and had previously been sampled by THORPE (1981). This minor spring actually feeds the Gordale Beck

system, and only restricted sampling took place until February 1982, when it was abandoned in favour of concentration upon the main elements of the 'cascading system' in the Malham area.

Higher Tren House borehole (HTH) (NGR SD 879667; altitude (well head) 395 m O.D.)

The borehole lies close to a fault (NNW-SSE), identified by O'CONNOR (1964) and near the junction of the Great Scar Limestone with the Silurian slates. It is the only borehole in the study area. It was sunk for domestic water supply in 1964, to a depth of 72 m, and the details recorded by the drilling company are presented in fig. 3.6. The borehole is lined to 14 m, water being extracted possibly from a thin band of limestone, but mostly from the shale beds. It has been suggested (J. Varney, pers. comm. 1981) that the borehole has been extended and exploded at the base since 1964, but no records are held by the original drilling company.

Water was pumped from the borehole by operating a float switch. Sampling took place between January 1981 and October 1982.

Smelt Mill sink (SM) (NGR SD 881660; altitude 385 m O.D.)

The nature of this small sinking stream has been discussed in section 3.2.1(d), although less is known about its upstream characteristics than about its positive and repeated tracing to Malham Cove. Samples were taken at the stream's crossing under the road, approximately 40 m upstream of the sink.

Tarn Outflow (TO) (NGR SD 894662; altitude 380 m O.D.)

Water flowing out of the Tarn is supposed by PITTY et al. (1979) to be in equilibrium with air temperatures, and PENTECOST (1981) attributes to the Tarn waters a long residence time of 'about 1 year', based on the recovery time after opening the sluice gates (A. Pentecost, pers. comm. 1981).

Sampling took place at the overspill slipway (plate III), where a fixed cross-section facilitated discharge determinations. This avoided complications in discharge measurement with the progressive sinking of the

Outflow prior to Water Sinks, 700 m downstream, and allowed a better consideration of the Tarn itself. Initial checks showed that the stable isotope composition of the water did not alter significantly downstream from the outflow point.

Malham Cove springs (MC) (NGR SD 898642; altitude 235 m O.D.)

The history of investigations into the nature of the springs at the foot of the 80 m high Cove (plate I) is discussed in section 3.2.1(d). Sampling took place close to the spring source, although discharge was measured at a point approximately 25 m downstream, where the flow was better contained in a channel.

Airehead springs (AHN, AHS) Investigations into the sources of, and the nature of transmission to, these springs were discussed in section 3.2.1(d). Airehead actually consists of two distinct springs, approximately 5 m apart and separated by a boundary wall. The two springs were monitored separately for the purposes of this study, although emphasis was placed on the most northerly, which is the larger.

Airehead North spring (AHN) (NGR SD 901622: altitude 190 m O.D.)

Sampling took place where the water emerged between boulders and turf. The head of the spring fell in dry weather and no flow was recorded in August 1982. A stage board (plate IV), installed in December 1981, was calibrated for discharge measurement.

Airehead South spring (AHS) (NGR SD 901622; altitude 190 m O.D.)

The behaviour of the smaller Airehead South spring is similar to the nearby Airehead North. This spring, however, always flowed, due to its slightly lower elevation.

Soil waters and cave drips

Turf Hill (THC, THD, THE) (NGR SD 878688; altitude 420 m O.D.)

Three soil moisture samplers were installed on the lower slopes of Turf

Hill, north of Knowe Fell, from October 1981 to June 1982. This was subsequent to the removal of a sampler from Knowe Fell (NGR SD 876687, altitude 445 m O.D.), after problems with access and interference by livestock. The samplers were located in an area of rough pasture, where drift overlies the Great Scar Limestone. They were approximately 3 m upslope (slope 1-2°) of an enclosed depression, thus aiming to sample the interflow contribution to such sinks. The siting on Turf Hill was chosen because it was considered representative of large areas on the lower slopes of Knowe Fell and Chapel Fell. Figure 3.7 shows the soil profile, compiled from nearby exposures (as in plate II), augering and from destructive coring at the end of the sampling period, together with sampler depths (35, 70, 80 cm). Two samplers were installed at the greater depth to allow for possible problems in obtaining the required sample volume, and in contingency for equipment failure.

Chapel Cave (CC) (NGR SD 881671; altitude 390 m O.D.)

Cave drips were collected in Chapel Cave, beneath a shallow depth of limestone, to represent percolation water derived from a partially bare area of limestone pavement. The location of the cave was noted by BROOK et al. (1976). Its entrance is on the side of a scar, and an old phreatic passage can be followed through a squeeze and into a small solution tube, where the passage is choked at 33 m from the entrance. A small stream flows at the back of the cave, probably towards the peat pool springs of Tarn Moss, and there is much sand washed in, similar to that found at Waterhouses spring. The drips derived from a near-vertical fissure in the roof, 2 m from the entrance and with mostly (about 80%) bare collapsed limestone pavement at the surface, approximately 3 m directly above this point. The fissure was 0.45 m above the floor at the east side of the cave.

After exceptionally heavy rainfall, 'bursts' are seen to occur on this section of hillside, and are referred to by TATE (1879). In January 1982,

water gushed from an opening, locally named Herbert Worm, approximately 5 m below Chapel Cave. Drips were sampled from April 1981 to September 1982.

Precipitation

Three sites were chosen for the collection of precipitation in the Malham area, to investigate any spatial variations of the isotopic input signals, especially any relationship with altitude. Specific details of the rainfall collectors used will be given in section 3.3.1.

Fountains Fell (FF) (NGR SD 869709; altitude 657 m O.D.)

This is the site of a Meteorological Office monthly reporting raingauge.

Malham Tarn Field Centre (MTFC) (NGR SD 894672; altitude 395 m O.D.)

Monthly sampling of rainfall for stable isotope and tritium analyses has taken place at this site , shown in plate VII, since October 1979 (THORPE, 1981). The staff of MTFC operate a third-order meteorological station at this site, which includes a daily reporting raingauge.

Malham Village (MV) (NGR SD 902613; altitude 185 m O.D.)

The sewage plant at this location, 500 m south of Malham village centre, is operated by the Yorkshire Water Authority. Restricted access to the site provides equipment protection in an otherwise much frequented area.

3.2.2 The Lambourn area, Berkshire

The location of the Lambourn study area is shown in fig. 3.1. This area of gently rolling chalk topography, as typified in plate VIII, lies on the dip slope of the Berkshire Downs, and its hydrology has been investigated as a pilot study area for the Thames Groundwater Scheme, which is reported by BRETTELL (1971).

The area under consideration, shown in fig. 3.8, constitutes the catchment of the River Lambourn, as defined by BRETTELL, before its junction with the River Kennet at Newbury. The catchment is elongate and orientated NW-SE; it is approximately 27 km long and 11 km at its widest part, and has a total area of 234 km^2.

Details of the area's geology, landforms and soils, climate and drainage, will be given as background to the choice of sampling sites, locational details of which follow in section 3.2.2(e).

3.2.2(a) Geology

An account of the detailed geology in the region of Hungerford and Newbury, and including the Lambourn area, is given by WHITE (1907), in a memoir explaining Geological Sheet no. 267 (New Series One Inch to One Mile). Specific aspects of the Chalk have been examined by later writers and will be discussed below.

The outcrops of solid strata are predominantly of Cretaceous Chalk, with a small area of Tertiary deposits towards the south-east corner of the catchment. Various drift deposits, the origins of which will be discussed below, cover about half of the solid outcrop (BRETTELL, 1971). These are shown, together with solid geology in fig. 3.9. A diagrammatic geological succession is given in fig. 3.10.

The Gault and Upper Greensand do not outcrop in the Lambourn area, but are hydrologically significant. The Gault clay acts as an aquiclude, separating the Chalk and Upper Greensand aquifers from the ones below. The Upper Greensand consists of ferruginous sands and sandstones, overlying a siliceous Malmstone (INSTITUTE OF GEOLOGICAL SCIENCES & THAMES WATER AUTHORITY, 1978). The Chalk forms the principal aquifer and may be divided into three lithological units:-

1. Lower Chalk: outcrops are restricted to narrow strips along valley bottoms and at the catchment head. This is the most argillaceous of the chalks, and the least significant for water transmission.
2. Middle Chalk: the outcrop is more extensive and the rock contains less clay than the Lower Chalk.

3. Upper Chalk: this accounts for about 80% of the Chalk outcrop (BRETTELL, 1971), and is the most significant in studies of groundwater movement. It is a pure, white chalk with abundant flints. At its base is a distinctive hard band, of yellowish limestone with phosphatic nodules, the Chalk Rock (WHITE, 1907).

Towards the southern end of the catchment, higher land is capped by outliers of Tertiary strata, mainly the sands, silts and mottled clays of the Reading beds; these are occasionally capped by small patches of London Clay.

Drift deposits are common, with complex interrelationships. Recent mapping performed by the Institute of Geological Sciences (BRETTELL, 1971) recognised slightly different classifications of drift from those originally used by WHITE (1907), although the proposed origins of the materials will only be briefly presented here. Three categories may be recognised:-

1. Clay with flints: this caps the Upper Chalk, mainly on high ground. It possibly constitutes the remains of the Reading Beds, with residual flints from the Chalk, reworked under periglacial conditions.

2. Coombe deposits: these comprise of soliflucted chalk rubble with flints, and are found in valley bottoms and lower slopes. The former 'river and valley gravels' of WHITE are continuous with this category, as coombe deposits are decalcified and undergo fluvial transport. Along the course of the perennial streams, the gravels are overlain by clayey alluvium or peat.

3. Plateau gravels: these are thin sandy or clayey flint gravels capping most of the patches of Tertiary strata.

The geological structure of the area is simple, with a regional dip of $\frac{3}{4}$-1° to the SSE or SE (in the northwest of the catchment). There is flexuring in the southeast corner of the catchment, with a gentle anticline, the axis of which strikes southeast (BRETTELL, 1971), parallel to the main river. WHITE

(1907) noted a locally high dip at Boxford (NGR SU 421719) of 23-25° SSE, which he attributed to pre-Tertiary movements. This feature and a sequence of hardgrounds in the same quarry exposure were later examined by WOODRUFF (1980).

3.2.2(b) Landforms and soils

The land in the study area exhibits typical rolling Chalk scenery. It rises to its highest along the crest of the escarpment to the north, to a maximum of about 259 m O.D., and along the divide with the upper part of the Aldbourne catchment to the southwest. The minimum altitude, at the river's exit point from the study area, is 77 m. The dip slope is dissected by valleys, which, excepting those of the Lambourn and Winterbourne, are normally dry.

Figure 3.11 shows the cross section of a chalk dry valley, and the soils and land uses typically associated with these features in the Lambourn area (modified from JARVIS, 1973; CURTIS et al., 1976). Alluvial soils supporting water meadow are frequently found adjacent to perennial water courses. Soils on the Tertiary inliers of Reading Beds and London Clays are generally podsols and stagnogleys respectively, associated with areas of heath or woodland. The soils of Berkshire are examined in detail by JARVIS et al. (1979), to which the reader is referred.

Table 3.4 shows a breakdown of land use for the study area. This is a composite of an assessment by the Meteorological Office and a field and aerial survey, both reported in BRETTELL (1971).

3.2.2(c) Climate

The climate of Berkshire is described by V. Bailey in JARVIS et al. (1979) as being equable. Winters are not severe and snow occurs only occasionally. The maximum rainfall expected (monthly maximum in November) is moderate, and drought is rare. Rainfall and evaporation over the catchment area have been investigated by the Meteorological Office for BRETTELL (1971).

In contrast to the Malham area, annual effective precipitation forms only approximately 40% of total precipitation. Annual average rainfall over the whole catchment, in the standard period 1916-1950, was 775 mm.

Within-catchment variations are slight, although rainfall is seen to increase generally with altitude (range 737-838 mm) and evaporation to decrease (range 546-509 mm) (BRETTELL, op. cit.). Over the wider region, in periods of northerly and north-easterly circulations, the relatively high ground of the Berkshire Downs tends to increase local precipitation amounts, with rain shadow effects to the south and south-west (STONE, 1983).

3.2.2(d) Drainage

Surface waters in the study area are limited to the main valleys of the River Lambourn and its tributary, the Winterbourne Stream, rising where the land surface intersects the water table. Both are, in part, bournes. The bourne head and normal source of the Lambourn consists of a series of springs in Lynch Wood, upstream of Lambourn village (fig. 3.8). During or after exceptionally dry periods, the upper course is dry, and migration of the source takes place quickly to the perennial head, near Maidencourt Farm, approximately 11 km downstream from Lambourn village. Records show the normal bourne head of the Winterbourne Stream to be in Chapel Wood, near North Heath, approximately 7 km above its confluence with the River Lambourn, while its perennial head is just downstream of Kimbers Copse, 1.6 km above the confluence.

When the water table is high, the surface drainage network extends up previously dry valleys. In particular, the valley which runs north from the Sheffords was observed to contain a stream for much of the sampling period. Also, the head of the River Lambourn extended up its two tributary valleys, beyond Upper Lambourn and north of Lambourn village, in February and March 1982. WHITE (1907) commented on the springs which commonly rise through

valley gravels and alluvium in the valley bottom, adjacent to the flowing River Lambourn. He assumed these to be derived from subsurface Chalk springs.

As a major aquifer for water supply in the U.K., a considerable amount of research has been directed towards the hydraulic properties of the Chalk. The rock matrix is characterised by a moderate to high primary porosity (0.15-0.40), small pore diameters (mostly less than 1 μm) and thus a very low primary permeability (EDMUNDS, et al., 1973). Jointing and bedding of the rock mass, however, may allow the more rapid transmission of water along fissures. Additionally, TOYNTON (1983) found a strong relationship between fracture patterns and hydraulic anisotropy in the Norfolk chalk. Preferential flow through the fissures may cause solutional widening through time or, as HEADWORTH (1972) suggests, with pumping of the aquifer.

Geohydrological investigations into the saturated zone of Chalk in the Lambourn area were undertaken by TATE et al. (1971) as part of the Thames Groundwater Scheme Pilot Study. They demonstrate, by borehole logging techniques, that the Lambourn Valley boreholes obtain very little water from beneath the Chalk Rock at the base of the Upper Chalk. Fissures were observed directly, by down-hole television cameras, to be horizontal or near-horizontal, and related to depositional features. OWEN & ROBINSON (1978) further analysed the depth distribution of these fissures and found the vertical limit of their development in the unconfined aquifer to be dependent principally on depth below the ground surface. Dependence on stratigraphy was only shown by a minor peak of fissure occurrences below 80 m, due almost entirely to the Chalk Rock.

From pumping tests, OWEN & ROBINSON found higher transmissivity values, at a common water level condition, in the valleys, whether dry or containing streams. These lateral variations are in keeping with those observed by INESON (1962).

The contribution of fissure flow to water transmisison in the unsaturated

zone has, however, been more controversial since the work of SMITH et al.(1970) This was discussed in relation to alternative hypotheses of water movement in the chalk unsaturated zone in section 1.4.3 , to which the reader is referred.

A mechanism which occasionally produces a fast response to rainfall in the River Lambourn was investigated by analysis of flow records by GASQUOINE (1978). This effect was most noticeable at Welford and Shaw gauging stations, and was attributed to runoff from the riparian area, with perhaps additional contributions from the Tertiary deposits at the bottom end of the catchment (fig. 3.9). No direct observations of flow into swallets identified by GASQUOINE (1978) at the southern edge of Snelsmore Common, nor of riparian runoff, have however been made. In this context, the suggestions of HEADWORTH (1972) in identifying the occasional response of water tables in chalk to rainfall (eg. by displacement or by percolation pressure) should not perhaps be excluded, since the combined response of a group of springs feeding the river may produce a similarly 'flashy' phenomenon.

Traditionally, flow through chalk has been regarded as near-Darcian, and only recently has its inhomogeneous nature been recognised. In the schema of SHUSTER & WHITE (1971), one would still expect to observe, however, low coefficients of variation of hardness, indicating a predominantly diffuse flow, at least in the initial stages of recharge. For springs emerging at the foot of the scarp slope of the Berkshire Downs, PATERSON (1971, 1979) noted low values for the coefficient of variation of calcium carbonate hardness, for example, 1.5% at Letcombe Bassett (NGR SU 372851) and 1.9% at Woolstone Springs (NGR SU 297872), and only small ranges of temperature, measured monthly over one year. It is possible, however, that greater variations may be observed on the dip slope, where the development of fissure flow, especially beneath valleys, has already been discussed. This particular phenomenon of the karstification of chalk is being examined in the Chiltern Hills by R. Fraser (pers. comm., 1982).

3.2.2(e) Sampling locations

Figure 3.9 shows the locations of sites where sampling took place of surface, ground and soil water, and of rainfall. Details will be given for each site, in the order specified in section 3.2.1(e). The standard sampling period for sites in the Lambourn area was from February 1981 to January 1983. Sites were chosen to coincide especially with locations where conventional hydrological information was available.

Surface waters

Head of the River Lambourn (SCE) Three positions of the head or source of the river were sampled, according to its stage:-

Lynch Wood (LW) (NGR SU 328793; altitude 130 m O.D.)

The River Lambourn normally rises in the 0.8 km stretch of Lynch Wood which commences approximately 0.3 km north of Lambourn village. The small spring chosen to represent the many springs in the wood was located near the southern end, rising at the foot of a Chalk cliff to the north-east, and feeding the lower pool in the system of fishing ponds here.

Riverside Cottage (RC) (NGR SU 328792; altitude 129 m O.D.)

When the spring in Lynch Wood was not flowing, the joint discharge of springs was sampled where the channelised river flows under the road at its exit from the wood.

Maidencourt Farm (MAID) (NGR SU 373759; altitude 113 m O.D.)

The River Lambourn was sampled at its perennial source in low flow conditions, when the bourne ran dry.

Welford (WEL) (NGR SU 411731; altitude 98 m O.D.)

The Thames Water Authority maintain a Crump broad-crested weir and autographic stage recorder at this site, gauging flow from a catchment area of 160 km^2. From studies of flow accretion and from river temperature records,

it is considered by BRETTELL (1971) that a large groundwater component is added to the Lambourn between East Shefford weir (NGR SU 390745), approximately 3 km upstream, and Welford. GASQUOINE (1978), however attributes the occasional 'flashy' response in this stretch to riparian runoff between the stations. Water samples have been collected at the Welford site since 1967 for tritium measurement, as part of the programme of environmental monitoring at the Isotope Measurements Laboratory, AERE Harwell.

Bagnor (BAG) (NGR SU 453694; altitude 80 m O.D.)

Thames Water Authority maintain a Crump weir and autographic stage recorder at this site, gauging flow from a catchment area of 49 km^2. This was the only location used for sampling the Winterbourne Stream, most emphasis being placed on the River Lambourn.

Shaw (SHAW) (NGR SU 470682; altitude 77 m O.D.)

Thames Water Authority maintain a Crump weir (plate IX) and autographic stage recorder at this site, gauging flow from the catchment study area of 234 km^2. GASQUOINE (1978) found the volumetric response of river flow at Shaw to rainfall to be particularly large, suggesting runoff from the nearby Tertiary deposits to be a contributing factor.

Groundwater

An intensive network of boreholes exists in the Lambourn area as a result of the Thames Groundwater Scheme Pilot Study. Five boreholes for sampling were chosen, to include:-

(1) both valley and interfluve sites

(2) observation boreholes with autographic water level records

(3) a borehole (Manor Farm) where groundwater was suspected to be in direct contact with river water.

Details of the boreholes in terms of location, depth, strata sampled and lining are given in Table 3.5. Sample collection from Ashdown Park borehole ceased in August 1982, when the housing was considered unsafe.

Soil moisture

Manor Farm, Great Shefford (MFA, MFB) (NGR SU 380755; altitude 108 m O.D.)

Soil suction samplers were installed in the area of water meadow adjacent to the River Lambourn (plate X), where alluvium overlies flinty river gravels in a chalk matrix. This site was chosen because an important part of the study in the Lambourn area was to assess whether a riparian contribution to riverflow could be identified isotopically. It was therefore important to monitor water in the riparian area, such as the Manor Farm water meadow, for any isotopic modification which might make it distinct for natural tracing purposes. Figure 3.12 shows diagrammatically the soil profile and sampler depths. Two samplers were installed, in contingency for small samples or equipment failure. The samplers were installed in July 1981 and functioned to the end of the study period (January 1983).

Precipitation

Warren Down Farm (WF) (NGR SU 357816; altitude 190 m O.D.)

Rainfall for stable isotope analysis was collected adjacent to the meteorological station already in operation at this site, representing input to the Lambourn catchment, over the large area of Chalk plateau. Sampling began in December 1981; the previous input values were derived from Lechlade, approximately 18 km to the north-west, with an overlap of one year being available for comparison.

Lechlade (LECH) (NGR SU 222990; altitude 72 m O.D.)

Collection of rainfall for stable isotope analysis has taken place at this site next to St. John's Lock since 1974. A daily raingauge, reporting to the Meteorological Office, is kept by the lock-keeper.

3.3 Sampling procedures

In this section will be presented the methods used for field sampling of the natural waters. Precipitation collection will be considered first

(section 3.3.1) followed by surface and groundwaters (section 3.3.2), and finally soil mosture and cave drips (section 3.3.3). Field measurements, for example of specific conductivity, are included in this section. Laboratory analytical procedures are reserved until section 3.4. Experimental investigations, carried out by the author, into the suitability of specific methods of water collection for stable isotope studies are reported in section 3.5. These methods concern the use of silicone oil and different raingauge styles in precipitation collection, shelf storage in different bottle types, the sampling of snow, and the extraction of soil moisture.

3.3.1 Precipitation

Precipitation (rain and snow) was collected for analysis of both stable isotope ratios and tritium concentrations, using separate collection procedures.

3.3.1(a) Collection of precipitation for stable isotope analysis

A variety of collectors were used in this study for the collection of precipitation as rainfall. This was because standard design rainfall collectors were not available for all locations, and also, since a variety of collectors have been used in other studies, it seemed important for future investigations to assess any differences which such inconsistencies may bring about. Interpretation of any modification of the isotopic input signal in rainfall in the terrestrial part of the hydrological cycle must depend upon adequate monitoring of this input.

The guidelines which exist for the collection of precipitation for stable isotope analysis were principally designed for stations within the IAEA/WMO worldwide network, which collect precipitation on a monthly basis. IAEA (1983) recommends the WMO standard raingauge to be used as a collector. The following sampling procedure is described:

> "After each reading of the gauge, but at least once a day, the precipitation sample is transferred to a tightly stoppered container large enough to accommodate the monthly amount of precipitation." (IAEA, 1983, p.10).

At the end of the sampling period, the bottle is shaken, and aliquots extracted for isotope analysis.

Evaporation processes within the precipitation gauge are recognised as a possible source of error, particularly in arid areas. Evaporation would change the isotopic composition of the water already collected and may lead to erroneous interpretation. An auxiliary, non-recording gauge is proposed to overcome such evaporation problems, and should have the features given below (IAEA, 1983, p.11):-

"(1) Smooth, clean surfaces - the outside may be painted gloss white
(2) A receiver bottle of heavy glass with a narrow neck
(3) The collector funnel extending to the bottom of the receiver
(4) The receiver installed below ground level
(5) A small quantity of non-volatile, low-viscosity, chemically inert oil which is immiscible with water, added to the receiver."

It is not clear, from these instructions, however, whether precipitation is emptied daily from the auxiliary gauge, or whether it is allowed to accumulate in the receiver (in which case a large capacity is required). Also, no threshold, in terms, for example, of monthly potential evaporation, is specified for the use of the auxiliary gauge, and no direct assessment of the magnitude of isotopic effects probable under different climatic regimes is to be found in the literature.

Reasons for the guidelines not being strictly followed in isotopic studies might include the expense of the standard precipitation gauge, the lack of clarity in the guidelines, and also the desire for non-monthly sampling, in which case comparability with IAEA/WMO published results may be of little interest. Are deviations from a standard procedure, specified in the guidelines, important for the assessment of the isotopic input signal? The possible sources of error, assuming a standard siting of the collector, will be examined below in terms of (a) isotopic variations due to differences in catch, and (b) isotopic variations due to evaporation within the gauge or collecting system.

(a) From micrometerological considerations, it is to be expected that the design of a raingauge, as examined by RODDA (1967), will affect its volumetric catch. This results from differences in contributions from splash-in and splash-out, and variations in catch with height above the ground surface, according to the wind velocity profile and turbulence around the rim of the gauge. The catch of precipitation as snow is a problem which has particularly concerned those countries in which snowfall is frequent and its volumetric assessment important in the estimation of water resources. Thus a standard Soviet precipitation collector is positioned 1 m above ground level, to avoid collection of drifting snow, and has a wind baffle around its rim (METEOROLOGICAL OFFICE, 1956; J. Seaton, written pers. comm., 1984). The British Meteorological Office standard raingauge, in comparison, has vertical walls and its rim 12" (28.8 cm) above the ground surface.

Since volumetric differences in catch between collector styles may be influenced by the type of precipitation occurring, eg. splash-in being most effective during heavy thunderstorms, it is also anticipated that isotopic differences may result from the use of different collectors. The probable magnitude of such differences is unknown.

(b) It is expected that evaporation of water from within a raingauge will vary as a function of raingauge design, of the ambient climate and of the frequency of emptying.

Standard raingauge designs have been developed to minimise internal losses due to evaporation of stored water. Gauges used in the tropics and sub-tropics may have all the qualities of the auxiliary, evaporation-suppressed gauge, listed previously. The use of an oil layer, however, remains cumbersome for an amount-recording gauge, creating both errors of measurement with the formation of an emulsion, or oil globules interfering with the reading of the meniscus level, and also unpleasant greasiness of interior surfaces.

The effectiveness of a layer of oil or paraffin in suppressing evaporation, however,has been shown many times. In certain cases, the additive is used to correct for a deficiency in the collector design. HAMILTON & ANDREWS (1953) in California, for example, found an oil layer (thickness 0.4 cm) to be as effective as a control of evaporation on a U.S. Weather Bureau gauge, minus the inner measuring tube, as would be a funnel. Experiments have been carried out with non-standard gauges by WICHT (1944) in Jonkershoek, South Africa, and by STARR (1930) in Amman, present-day Jordan, and both found paraffin to reduce considerably evaporative losses in these semi-arid areas. NORUM & LARSON (1960), in the humid continental climate of Minnesota, U.S.A., found average summer evaporative losses from a standard U.S. Weather Bureau gauge to be of the order of 0.008 cm.day. Addition of a few drops of hexadecanol (cetyl alcohol) in methyl alcohol reduced this loss by 24%. The British Meteorological Office standard gauge differs fundamentally however, from the U.S. Weather Bureau gauge in that the receiver is sunk into the ground, providing insulation against solar heating, whereas the latter gauge is raised off the ground, on a stick, and therefore of a style more susceptible to evaporative loss.

As an illustration of the importance of the frequency of emptying the raingauge on evaporation, particularly in an arid climate, WICHT (1944) found a 5.7% loss over a year from monthly readings When compared with the sum of daily readings, ie. the greater the frequency of emptying, the lower the loss incurred.

Quantitative evaporation from standard British Meteorological Office gauges, in the temperate maritime climate of the U.K., if complying with their specification, should be minimal. It is the use of odd receivers and funnels in careless combination, and without proper consideration of catch and

evaporative loss, however, which incur the greatest risk in studies of stable isotope hydrology.

It is important to note that the stable isotope composition of the sample collected is only affected if there is a loss of water vapour which is isotopically different from the remainder of the sample, ie. when isotopic fractionation occurs. A complete evaporative loss, or a leakage of water from the receiver, are not as important in isotopic terms, if a reliable check gauge is available for volumetric measurement. (Complete loss is most likely to occur when collections are small, possibly too small for analysis, although it is recognised that if such small samples were to be isotopically very different, then any attempt to specify a weighted isotopic average would be accordingly in error by that sample's exclusion.) If evaporation occurs within the raingauge, but all condensation is retained within the gauge and can be incorporated in the water sample, then no net isotopic change should occur. Exchange between oxygen in the precipitation sample and CO_2 in the air space above however, is possible, and will be considered in the experimental section (section 3.5).

Monthly collection of precipitation in this study

Standard Meteorological Office raingauges were preferred for use, but their availability was limited, and these not all of the same design. Additionally, monitoring of stable isotopes in precipitation had been undertaken by the Harwell Isotope Measurements Laboratory since January 1974, under the aegis of R.L. Otlet, using a cheaper, laboratory-made collector. This collector will be referred to as the Harwell collector. It consists of a 1.3 litre polythene bottle as receiver, with polythene funnel (11.5 cm diameter), set in the case of a Dewar bucket, as illustrated in fig. 3.13. Approximately 15 ml of silicone fluid (Dow Corning, 200/200cs) is added to the receiver, providing a film about 2 mm thick, to suppress evaporation. Monthly samples have been collected at Lechlade since 1974 using this collector. This

project aimed to continue this long-term isotopic record, and therefore the Harwell collector was retained, but also subsidiary studies initiated to assess the performance of this collector relative to other, more standard, styles.

On Fountains Fell in the Malham area, an Octapent style, 1270 mm capacity, standard Meteorological Office monthly storage gauge has been operational as a monthly reporting raingauge since 1963. It appeared impracticable, after discussions with staff of the Malham Tarn Field Centre who were responsible for the continuation of the rainfall record, either to (a) add an oil film to the reporting raingauge, or (b) install an auxiliary collector nearby (due to the remote location, and the requirement of a robust and expensive second gauge). It was decided, therefore, to accept sample aliquots directly from the established storage gauge, with the provision that an experiment be initiated to compare the collection of precipitation, in standard raingauges, with and without the use of an oil layer.

Collecting vessels used for comparison in the Malham and Lambourn areas are listed in table 3.6, with examples shown in figs. 3.13 and 3.14, and in plate XI. The dates of their installations reflect, to a large extent, the times of obtaining the standard raingauges.

A 2.5 litre glass cylinder with glass funnel had previously been used for the collection of precipitation, under a layer of silicone oil, by P.M. Thorpe, from September 1978 to January 1981 (THORPE, 1981), at the Malham Tarn Field Centre site. The style had been favoured because the glassware was easy to clean, and presented a smooth surface, for minimum droplet retention. It was considered for this study, however, that the catch might be biased by its non-standard height above the ground, and its particular aerodynamic form. Also, loss of sample due to freezing in the glass cylinder and subsequent breakage was a proven danger in using this design. The record of stable isotopes at Malham Tarn Field Centre was continued, therefore, using more standard collector styles.

The decant procedures used for monthly precipitation samples are included at the end of this section. Results of the experimental use of different precipitation collectors are presented in section 3.5, together with recommendations for stable isotope collection methods for future studies.

Weekly collection of precipitation in this study

Weekly sampling of precipitation was carried out by the daily meteorological observers at Malham Tarn Field Centre and at St. John's Lock, Lechlade.

Provision was made for the observer at each location to empty the full amount of measured rainfall into a 1.3 litre polythene bottle, the screw-top lid of which was then sealed tightly. Accumulation of daily samples took place in each bottle over a period of one week. The bottles were chosen to accommodate all but the most exceptional weekly rainfall totals (in retrospect, approximately 99% of total), and to ensure no loss of sample due to bottle breakage, should sample freezing take place. The bottles were generally kept outside, near the daily recording gauge, during their week of use.

When precipitation fell as snow and, at the time of observation (09:00 G.M.T. daily), snow remained in the funnel of the reporting raingauge, a specified procedure was followed:-

(1) The amount of rain entering through the raingauge was recorded and the rain emptied into the weekly storage bottle.

(2) A sample of fresh snow, which had fallen since the last time of observation, was scraped into a 30 ml glass bottle, the top sealed, and the contents left to melt slowly indoors. After the observation, snow was swept clear of the surface sampled, in the case of Malham Tarn Field Centre, the roof of the Stevenson Screen.

(3) Snow and/or ice lodged in the funnel of the raingauge was quickly

melted out for volumetric measurement, possibly using the addition of a known volume of warm water in accordance with recommendations made by the Meteorological Office (1981, Snow measurement (A), p.6). This melted snow was discarded, since isotopic modification during rapid melt was suspected, and was certain with the addition of heated tap water.

Final isotopic values for weeks when snow was collected in this manner were computed by weighting rainfall and snow stable isotope data for their attributed rainfall depth (mm) amounts. An investigation into the actual isotopic effects of rapid melt was carried out during this study (see section 3.5 for results).

Decant of monthly and weekly samples

All monthly and weekly samples stored in polythene bottles were decanted as soon as possible after sampling, and always within 6 weeks. An experiment to investigate isotopic modification with storage in various bottle types and volumetric combinations was carried out from July 1981 to July 1982, and is reported in section 3.5.

On decanting, the depth of monthly or weekly samples in the bottle was recorded as a possible cross-check, prior to the extraction of a 25-30 ml aliquot for stable isotope measurement. The total amount of sample collected was measured volumetrically, and the equivalent rainfall depth calculated.

Where an oil layer had been used to prevent re-evaporation of sample within the raingauge, the aliquot was obtained from below the oil layer using a 25 ml pipette. The pipette was rinsed thoroughly with the water being sampled, as was the receiving 30 ml sample bottle (this in cases of all samples, with or without oil).

Samples waiting (to be decanted) were stored wherever practicable in cool, constant temperature locations to minimise the possibility of evaporation. Care was taken to mix thoroughly the sealed sample where internal surface condenstation droplets were identified, prior to being decanted.

Smaller samples of less than 25 ml total (2 mm through a standard 5" diameter raingauge) were the most likely to have undergone significant isotopic changes during storage in larger polythene bottles, and were treated as the most suspect. Such samples were decanted in toto into fresh 30 ml glass bottles.

Details of routine sample storage are given in section 3.3.2(c).

Within-storm collection of precipitation

Initially, within-storm rainfall collection was performed manually, at variable time intervals. A polythene bottle arrangement was used, with no outer container,but with the feeding tube leading to the base of the bottle as already shown in fig. 3.13. Where within-storm sampling was carried out under cool conditions, with high relative humidity, as was usually the case, no silicone oil layer was used, since in the short period of exposure allowed, re-evaporation effects were expected to be minimal. Also this method was much preferred for ease of handling, oil inevitably causing slipperiness on bottle surfaces, and lubricating the screw cap seal of the 30 ml glass bottles in which samples were stored.

An automatic sampling system was proposed in order to examine the finer structure of rainfall within storms, over periods of several days. In addition, such a system could be designed to match the sampling interval of the automatic stream sampler (see section 3.3.2), for cross-correlation of isotopic results through a time series of storm sampling, although, in fact, the automatic rainfall sampler itself was introduced rather late in the programme of storm hydrograph sampling to achieve this objective.

Several alternative designs for an automatic rainfall sampler were considered, and the specifications for each are compared in Table 3.7. The basic requirements for an automatic rainfall sampler were:-

(1) A constant time-interval sample change mechanism. (This was decided upon, instead of a constant volume collector, as in a tipping bucket design, for comparability with the 2-hourly stream samples being taken over storm events).

(2) A minimum running time of at least 2 days to be worthwhile (the estimated limit of endurance for regular manual sampling by one person).

(3) Incorporation of a standard raingauge funnel aiming for comparability of catch with a standard recording raingauge.

(4) Direct use of 30 ml glass bottles for sample collection, to avoid decanting problems of small volumes. (This bottle capacity, however, limits sample retention to an equivalent of 2.4 mm rainfall if a 5" diameter funnel is used. This was considered acceptable if mixing of samples in the bottle could be provided, and allowance made for the collection of overflow.)

(5) A rotating gravity feed mechanism into a fresh collecting bottle to minimise cross-contamination.

(6) A device to minimise evaporation of sample out of the glass bottle, once collected.

The Rock & Taylor model was chosen, offering the most flexibility and a mechanism already proven under field conditions. The purpose-built automatic rainfall sampler is illustrated in plate XII. Discussions concerning the design of an automatic rainfall sampler began with Rock & Taylor in April 1982 and the sampler was ready for use in July 1982.

The rotating arm moves one position clockwise at a pre-set interval or delay, its distributing tube feeding a series of 52 small funnels, 48 of which lead to standard 30 ml glass bottles, screwed into caps fixed permanently in a grid on a perspex plate. The drop of 13 cm between funnels and perspex plate

allows for the free flow of water down the connecting tubing, which is clear and flexible, for easy cleaning (using pipe cleaner, tissues and hairdryer where necessary). This tubing penetrates into the bottles. Although air venting must occur when the bottle is being filled (most probably via screw holes in the bottle caps, if not back up the tubing), the actual exposure of the sample to air, once collected, is limited, and evaporation effects from this design are expected to be minimal, especially over the short period of sampling for which it was designed.

The spare funnel positions in the top distributing circle were used as follows; one (into a polythene bottle) for water collection prior to firing (ie. during the delay period), one (into a polythene bottle) for water collection after the end of the sampling cycle, over which the distributing arm would remain until tended to, and the remaining two positions had the small funnels cut away so that any overflow from other positions would drain down these into a single polythene bottle. The 500 ml polythene bottles contained a silicone oil layer during summer months when isotopic modification of the samples, offering a relatively large area for evaporation and exchange, was most likely. This equipment was powered by a 12V DC sealed rechargeable lead acid battery.

The least satisfactory aspect of the design was the influence of the box shape (0.41 m high x 0.60 m long x 0.37 m wide) in creating local turbulence and so affecting the catch. (A more permanent use of the equipment could have solved this by almost entire burial of the unit.) However, a comparison of 2-hour catches and amounts recorded on a nearby hyetograph show a good agreement for the events studied (as exemplified in section 4.2.3).

3.3.1(b) Collection of precipitation for tritium analysis

Tritium (^3H or T) is the radioactive isotope of hydrogen. The unit of its measurement is the TU (tritium unit), where one TU has an isotopic ratio ($^3H/^1H$) equal to 10^{-18}. Tritium occurs in precipitation, as HTO, from two

sources: (1) from the interaction of cosmic-ray-produced neutrons in the upper atmosphere with nitrogen ($^{14}N + n \rightarrow {}^{3}H + {}^{12}C$), and (2) from detonation of thermonuclear devices, since 1952. This second source caused concentrations to reach a peak of three orders of magnitude greater than natural background levels (5-20 TU, PAYNE, 1983), in 1963. Levels in precipitation have since declined, but exhibit seasonal and year-to-year variations, according to the 'turn over' of the troposphere.

Tritium in water, offers unquestionable advantages as a tracer in the study of groundwater movement, in following the water itself (LIBBY, 1961). Its input is areal, in natural precipitation, and a half-life of 12.35 years allows for 'dating' of waters, and therefore inference of hydrological processes, over relatively short periods (as compared with, for example, carbon-14, which has a half-life of 5730 years). Decay of bomb-produced tritium to levels similar to those found in precipitation today, however, make detailed interpretation of groundwater levels more problematic than in times closer to the tritium level peak. Accordingly, interpretation of groundwaters is only certain, in the present mid-latitude, maritime, Northern hemisphere environment, if sampled tritium levels are lower than 1 TU. Water may then be categorised as being of pre-bomb (ie. pre-1952) origin (FONTES, 1983).

In the present study, precipitation was collected over monthly periods at Malham Tarn Field Centre for tritium analysis. This continued work already begun by P.M. Thorpe in 1978 (THORPE, 1981).

The collector used is shown in fig. 3.15 and also in plate VII. Large samples (at least 500 ml) are preferred for tritium analysis, although measurement is possible on much smaller samples (down to 100 ml) with a corresponding loss of accuracy. A large funnel (0.41 m diameter) and large volume (25 litre) vessel are therefore used. The collector is partially sunk, for stability.

Due to the very low concentrations of the tritium present in natural

waters and the relatively high error of measurement of ±5% (compared with ±0.01% for $^{18}O/^{16}O$), neglible evaporation effects are likely to be detected in tritium unless a very significant proportion of the water is driven off. At Malham Tarn Field Centre, a rough measurement of volume was taken, using a metre rule as a dipstick, prior to rinsing twice and then filling a fresh glass bottle with sample for tritium analysis. Details of tritium sample storage are given in section 3.3.2(c).

3.3.2 Surface and groundwaters

Waters were sampled primarily for isotope analysis. Measures of the basic conditions of water chemistry and of physical hydrology at the time of sampling were made in order to (a) assist in the interpretation of the stable isotopes by describing the state of the system at the time of sampling, and (b) to provide the 'conventional' hydrological data, a comparison of isotopic information with which is a fundamental objective of this study (section 1.2).

The basic field measurements were of temperature, discharge/standing water level, specific conductance, hydrogen activity and alkalinity; discussion of the techniques employed follows in this section. Laboratory procedures will be presented in section 3.4.

Of the field measurements, physical hydrological measurements will be considered first, and then chemical analyses and sample collection for subsequent analysis.

Measurements of temperature and water quality were made on samples taken directly from the stream, or, where indicated, with instruments placed in the stream itself. Measurements of borehole waters, where there was open access from above, were made on water either from a series of samples taken using a simple bucket dipper (fig. 3.16(a)), or using a remote-firing depth sampler (fig. 3.16(b)). For the case of Higher Tren House borehole, which is the only pumped borehole sampled, measurements were taken after water had been pumped

from the borehole for approximately 2 minutes, which was considered adequate to flush the pipes of above ground water storage. The excess water was added directly to the domestic gravity feeder tank.

Depth samples were taken of open boreholes as recommended by PAYNE (1983) to investigate any stratification effects, either due to stratification in the phreas or due to evaporation effects at the standing water surface. This took place on three occasions only (March, April, July, 1981), but monthly down-hole temperature profiling was intended to assist in interpretation of the depth data obtained.

The procedures reported in this section are generally those employed during routine monthly sampling visits. Shorter period sampling studies are reported, for the more hydrologically responsive Malham area, in Part 4. Within-storm sampling generally took place at two-hourly intervals, using a Rock & Taylor automatic stream sampler (Multipurpose Liquid Sampling Machine), installed at the Waterhouses weir site. Continuous discharge measurements were available, and spot checks made of flowing water temperature; the field chemistry procedures described below, however, were in this case carried out under laboratory conditions.

3.3.2(a) Physical hydrological measurements

Temperature

Water temperature was normally measured using a calibrated mercury-in-glass thermometer, requiring 100 mm or full immersion and with ranges from $-10^{o}C$ and from $-5^{o}C$ to $+50^{o}C$ respectively, for the two models employed. Readings were accurate to $\pm$ $0.1^{o}C$, although to take into account local variations in water temperature, an error bar of $\pm$ $0.2^{o}C$ is perhaps more realistic. A minimum of five minutes was allowed for instrument response, prior to reading.

For stream measurements, the thermometer was placed directly in the water, where the flow was considered to be most homogeneous, and away from

stagnant pools. For springs, it was placed as close as possible to the point of water emergence from the ground.

Temperature readings of borehole samples were made as soon as possible after extraction, with the appropriate thermometer immersion, in a polythene vessel. A cross-check of temperature was provided for the open-access boreholes (not Higher Tren House) from the down-hole temperature profile measurement made using the temperature probe of an Ott contact gauge (type KLT100). Using this method, water temperature measurements were normally possible to $\pm$ 0.1^{o}C. Checks were made between the Ott temperature probe (range 0-20°C) and a mercury-in-glass thermometer, both prior to sampling and in the field. A satisfactory agreement was always found.

Discharge (of surface waters)

Discharge measurements were made of open channel flow wherever practicable at sampling sites, and where no Water Authority measurements were available.

The velocity-area method, described in British Standard 3680 Part A (BRITISH STANDARDS INSTITUTE, 1980), was followed as closely as possible towards the end of the study, but early measurements (up to December 1981) incurred larger errors, due to less accurate measurement of width and the smaller number of panels used. With most of the streams sampled falling in the width range 0.5-2 m, between 5 and 8 point velocity and depth measurements were normally taken. Point velocities were measured using an Ott current meter (type C2), on a 9 mm wading rod with a calibrated propellor (reference 1-55448, for most velocities, but reference 3-80077 in high flows, say in excess of 0.9 ms^{-1}). Single point velocity measurements were taken at 0.6 of the depth below the surface, over a period of 50 seconds. This was considered an adequate estimate of mean vertical velocity when depths of water were less than 0.60 m (GREGORY & WALLING, 1973, p.127).

An estimate of error in discharge measurements for this study under

'normal' conditions was calculated following the procedure of BS 3680 Annex (sic.) E. A total random uncertainty in the measurement of discharge of $\pm$ 14% was found (at the 95% confidence level).

When discharge was low, measurement was occasionally made using surface floats in dissipated flow (after BRITISH STANDARDS INSTITUTE, 1980, p.7), or by complete collection of discharge for contained flows (the 'volumetric method' of NEWSON, 1979, p.22). In the latter case, flow was collected, over a timed perid, using large heavy-duty polythene bags, with subsequent volumetric measurement of the water. Results from this method were found to agree closely with discharge calculations from a single mid-channel velocity measurement, with no flow assumed at the channel margins. A stage board was established at Airehead Spring North (on 4.12.1981), shown in plate IV; a rating curve was used to estimate discharge, after a period of calibration through a range of flows, shown in fig. 3.17(a), using a log-log plot as advised by GREGORY & WALLING (1973) to obtain a straight line relationship.

In order to support intensive within-storm (hydrograph) sampling studies, and to assess hydrological conditions between and especially prior to monthly sampling visits, a reference station with continuous discharge monitoring was established. The site chosen was Waterhouses Spring. This site was of particular interest since it was considered to be fed mostly by percolation waters (TERNAN, 1971) and yet was known to exhibit considerable discharge variations in response to precipitation. A thin-plate rectangular weir and a vertical Munro stage recorder, with check stage board, were installed downstream of Waterhouses Spring, in July, 1981. The installation at Waterhouses is illustrated in figs. 3.18 and 3.19 and plates V and VI. The design and maintenance of the weir were in general accordance with BS 3680 Part 4A (BRITISH STANDARDS INSTITUTE, 1981) and with BOS (1978).

Weir maintenance was required approximately once every 3 months. This included vegetation and sediment clearance, identification of erosion

problems, provision of extra sandbags (where appropriate) and flushing out of the stilling well. Charts were changed on a fortnightly basis by staff of the Malham Tarn Field Centre. Particular attention was taken to the discharge measurement of Waterhouses stream, in order to derive an accurate rating curve for the weir. This was necessary because, over a significant range of flow, aeration of the weir plate was found to be inadequate, and deviations from a structure rating curve were expected (BOS, 1978, p.45). The empirically derived rating curve is shown in fig. 3.17(b).

Borehole standing water level

It was only possible to measure the depth to standing water level in boreholes which had open access from above (not Higher Tren House). The Ott electric contact gauge was used to measure water level depth, and also depth down the measured temperature profile, in the free water of the borehole, as already mentioned for temperature measurement. Readings from the graduated tape were accurate to $\pm$ 1 cm (in up to 100 m), measurements being taken to a reference level (of known height above O.D.), at the borehole head.

3.3.2(b) Chemical measurements

Field measurements of water chemistry made on a regular basis are described below. It was considered important to measure pH and alkalinity in the field, since these properties, and, to a lesser extent, specific conductivity, are liable to modification with sample transportation and storage.

Specific conductance

> "Electrical conductance is the ability of a substance to conduct electrical current. Specific conductance is the conductance of a cube of substance 1 cm side (conductivity per centimetre)".

(EDWARDS et al., 1975, p.23).

The S.I. unit of conductance, the reciprocal of electrical resistance, is the siemens (S), and specific conductance for natural, non-saline waters may be expressed in $\mu S\ cm^{-1}$.

Specific conductivity was initially measured using a Simac analogue conductivity meter (ref. 1613), but from 27.11.1981 a PTI-10 Mini-Digital conductivity meter was used. Readings using the Simac meter had an accuracy of $\pm$ 5 μS cm^{-1} and erratic calibration, in comparison with the specified accuracy of the PTI meter of better than $\pm$ 0.5% on all ranges and repeatability in the field of $\pm$1 μS cm^{-1} found in the range 0-2,000 μS cm^{-1}. Solutions of 0.01N KCl (1 413 μS cm^{-1}), and 0.005 N KCl (718 μS cm^{-1}) in addition to distilled water (<5μS cm^{-1}) were used for periodic calibration checks of the instruments. Automatic temperature compensation (of 2% conductivity per ^{o}C) referred readings to 25°C for both models of meter.

Conductivity measurement was normally made by placing the probe (containing two 1 cm^2 electrodes, set 1 cm apart) in the stream or in a beaker of sample water, if flow was too vigorous for a reliable reading. Care was taken to flush out the conductivity probe after use, with distilled water, to prevent the build up of deposits between the electrodes.

Hydrogen activity (pH)

pH may be defined as the negative logarithm to the base 10 of hydrogen ion activity in a solution, ie.

$$pH = -\log_{10}[H^+], \text{ or } \log_{10}\frac{1}{[H^+]}$$

The pH of a neutral solution is 7, and the range of typical levels in natural waters may be given as pH 4 (acidic) to pH 9 (alkaline).

COOK & MILES (1980, p.44) state that the

> "...reliability of pH data depends upon a combination of several factors, including: stability and reliability of the pH meter; response characteristics of the electrode; accuracy of the buffer solutions; ionic strength of the samples and adequate temperature control."

Initially, the stability and reliability of the meter were of greatest concern, using an EIL portable pH meter (model 30C), readable to $\pm$ 0.05 pH units, but results were only poorly reproducible. Subsequently (December

1980), a more reliable meter, the Knick Portatest 9, was obtained, and more attention could be paid to other sources of measurement error.

Calibration of the pH meters took place using laboratory prepared EIL pH 7 and pH 9.2 buffer solutions, with instrument adjustments to take into account the temperature of the solution. This was carried out both before field sampling and during the sample run.

pH measurement of a water sample was made in a beaker, with temperature as close as possible to that of the water source (eg. with beaker in the flowing streamwater) in consideration of the effects of temperature on the determination of pH, noted by EDWARDS et al. (1975). Allowance was made for temperature equilibrium of the pH electrode with the sample, until a steady reading was obtained. Frequently, a fresh sample was then measured as a check. Manual adjustment for the temperature of solution was made on the meter.

Readings were generally reproducible to $\pm$ 0.05 pH units (Knick meter), but less reproducible in waters of low conductivity (low ionic strength and buffer capacity), and those near saturation or super-saturation with respect to $CaCO_{3(aq)}$, where deposition of calcite sediment on the electrode was suspected (as noted by THORPE, 1981, p.35).

Alkalinity (carbonate hardness)

Carbonate hardness is part of the total hardness of a water, and represents the proportion of calcium and magnesium salts present in the water in the form of carbonates (CO_3^{2-}) and hydrogen carbonates (HCO_3^-) (GOLTERMAN et al., 1978). Considerable confusion has arisen over the terminology in the reporting of alkalinities, with a variety of methods for determination available, including the use of branded indicators with differing end points. This problem is discussed by ROSE (1983), who prefers the technique-descriptive definition of (total) alkalinity as (p.21):-

> "a measure of tritatable base content, specifically the sum of all entities (ions and molecules) that can be titrated with a standard acid..."

in units of ppm as $CaCO_3$. As an indication of discrepancies in the literature, a technique identical to that described by ROSE is listed by COOK & MILES (1980) as a procedure for the measurement of 'bicarbonate' (in units of mg/ml HCO_3^-), with the note that although (p.11)

> "...such a procedure strictly determines total alkalinity,... for many groundwaters, the dominant contributors to (total) alkalinity are the carbonate species."

It was considered important in this study to measure alkalinity at the site of sampling, since outgassing or ingression of CO_2, out of or into the sample (according to sample pCO_2 values with respect to atmospheric pCO_2), is likely to occur in sample transportation and/or storage. This has been found, for example by CRABTREE et al. (1981), to significantly affect alkalinity values. A Merck Aquamerck Carbonate Hardness reagent kit enabled the field measurement of titration alkalinity. A micro-titration of hydrochloric acid into 5.0 ml of water sample was performed to pH 4.3. A mixed indicator was used, which exhibited a colour change from blue (via grey) to red, at this pH value. A calibrated syringe was introduced into the kit, to improve volumetric measurement of the sample. Care was taken to rinse out the receiving vessel prior to titration, and to expel any bubbles from the graduated titrating pipette.

Each titration was repeated, improving the precision of the results expressed as the standard error of the mean, by $\sqrt{2}$ (TOPPING, 1972). Reproducibility was generally better than $\pm$2.2 ppm HCO_3^- or $\pm$ 3.6 ppm $CaCO_3$ (these are equivalent units, since both CO_3^{2-} and HCO_3^- are measured together). Had the water chemistry been of principal interest in this study, it is recognised that further improvements in precision in this method could have been made, for example, by the adaptation of the micro-burette method of LAURITZEN (1981).

3.3.2(c) Sample collection and storage

Particular procedures were adopted in sample collection and storage,

prior to analysis, for particular constituents in the water, viz. stable isotopes of oxygen and hydrogen, stable isotopes of carbon, radioactive tritium and chemical species.

Sampling vessels were well rinsed with the test water before use. Samples from streamwaters were taken from the main flow channel, in an attempt to ensure good mixing, and spring samples taken as close as possible to the principal outlet. In accordance with PAYNE (1983), care was taken to avoid sampling from standing pools of water near a spring, except where that was specifically the objective, since these are likely to have a modified isotopic composition as a result of evaporation and atmospheric exchange.

Stable isotopes of oxygen and hydrogen

Water was sampled using 30 ml glass bottles of the Universal type, with brass screw-thread caps. Glass was preferred to polythene to minimise the problems of molecular diffusion and exchange through the bottle walls, with extended storage. Only a small air gap was allowed in the bottle, for liquid expansion with changes in temperature. The bottles were tightly sealed, and Parafilm (paraffin wax) tape added as an extra precaution.

Bottles were stored in fairly constant conditions of temperature (approx. 20°C) and relative humidity (regulated to 60%) in the Harwell Laboratory, both prior to and subsequent to analysis.

Stable isotopes of carbon

Measurement of the stable carbon isotope ratio ($^{13}C/^{12}C$) of dissolved inorganic carbon in ground and surface waters is included in this study as an indicator of water source and also of flow dynamics. Different sources of carbon have distinctive isotopic concentrations, which may be expressed in δ notation ($^{o}/oo$) with respect to the PDB standard (see Appendix A). Atmospheric CO_2 has a typical $\delta^{13}C$ range of -7 to -9 $^{o}/oo$ (MOOK, 1980); marine limestones vary narrowly about 0 $^{o}/oo$; soil CO_2 levels are approximately -26 $^{o}/oo$, for Calvin cycle plants, typical of the mid-latitude region. Flow

dynamics may be inferred from the relative contributions of these sources to the final water $\delta^{13}C$ level. Importantly, HARMON (1971) was able to characterise the "open" and "closed" carbonate dissolution systems of GARRELS & CHRIST (1965) (see fig. 1.4) in terms of $\delta^{13}C$, providing useful extra hydrological information.

In this study total carbonates for $^{13}C/^{12}C$ analysis were precipitated out of water samples, in the field, by the formation of insoluble strontium carbonate ($SrCO_3$) in a strongly alkaline solution, as recommended by OTLET (1972). The reagent used was strontium chloride ($SrCl_2$) dissolved in 85% w/v ammonia solution, in the proportions 20.0 g in 50.0 ml respectively. This clear solution was prepared in the laboratory prior to sampling, and 30 ml aliquots decanted into tightly sealed glass bottles (to minimise the possibility of ingress by atmospheric CO_2). This amount was then added in the field to a 1 litre sample of water, in a 1.3 litre polythene bottle. The bottle was well sealed, adding Parafilm tape, and the precipitate allowed to settle.

This precipitation process may be expressed:-

$$SrCl_{2(aq)} + HCO_3^-{}_{(aq)} + NH_4^+{}_{(aq)} \rightarrow SrCO_{3(s)} + 2H^+Cl^-{}_{(aq)} + NH_{3(aq)}$$

Laboratory recovery of the precipitate was normally carried out within a week, and never more than four weeks after sampling. The clear supernatant was siphoned off, and the precipitate filtered out onto a pre-weighed glass sinter filter (by water jet vacuum), and washed through with distilled water to prevent any precipitation of carbonate derived from atmospheric CO_2. (This was possible because the strontium reagent was always added in excess.) The precipitate was oven-dried at 105°C; roasting to remove organic materials was not considered necessary, as shown by THORPE (1981). The precipitate was then weighed and powdered, before being stored in sealed (screw top) glass sample

tubes. The recovery of carbonate procedure used is comparable with that reported by PEARSON et al. (1978), in the order of

"....filter, wash, dry, homogenise." (p.1800).

The precipitation method outlined above, however, contrasts with that used for the precipitation of carbonates for carbon-14 radiometric assay, for which the reagent used is barium chloride in carbonate-free sodium hydroxide, with ferrous sulphate to aid flocculation (OTLET, 1977; COOK & MILES, 1980; THORPE, 1981). The precipitation samples obtained by the two methods, were referred to by THORPE as bulk (for carbon-14) and specific (for carbon-13) samples. Original motives for the distinction of method for the different isotopes are not clear.

Barium precipitation has been quite widely used for carbon-13 analyses (eg. by FLEYFEL, 1979; BATH & DARLING 1981). FONTES (1983), in giving guidance on nuclear techniques in hydrology, shows no preference between barium or strontium salts as reagents. Workers in the U.S. Geological Survey, however, have preferred the strontium method for <u>total</u> dissolved inorganic carbonate collection, used for example by PEARSON et al. (1978) and by HAAS et al. (1982). This strontium technique is, however, less practicable on the scale of sampling for carbon-14 measurement, which requires the processing of 100-200 litres of water to obtain approximately 100 g of ($BaCO_3$) precipitate, used in traditional measurement methods (OTLET, 1977).

Doubts concerning the comparability of results using the two precipitation methods arose in THORPE's (1981), work and in hydrological studies carried out by the Institute of Geological Sciences (R.L.F. Kay, pers. comm., 1981), and further experimental work is required to resolve this issue and assess its implications for the interpretation of carbon isotope data. The strontium method was used consistently in this study, with the objective of obtaining results which are internally comparable. Experimental work was carried out, however, by the author and by staff of the Harwell Laboratory,

and indicated ingress of atmospheric CO_2 at the filtering stage of the strontium technique to be the most critical, causing $\delta^{13}C$ deviations of up to 1 $^{o}/_{oo}$. Particular care was taken in this stage of the operation to minimise the introduction of a variable error, but this must be borne in mind in addition to the measurement error (section 3.4.1) when interpreting results.

Tritium

Tritium samples were collected in 500 ml borosilicate glass bottles, to minimise molecular diffusion and exchange through the container walls. The bottles were filled with only a small gap for expansion with temperature. The bottles were sealed tightly, and extra Parafilm tape added, as advised by OTLET (1977). The filled bottles were particularly susceptible to breakage with sample freeze (metal-capped bottles were able to 'give' with freezing), and care had to be taken to store in temperatures above $4^{o}C$. The bottles were protected from exposure to sources of artificial tritium, such as are found in luminous watches, according to the recommendations of IAEA (1983, p.11).

Water chemistry

Sampling was intended for the analysis of the major ionic species. The cations, Ca^{2+} and Mg^{2+} were of principal importance in the carbonate waters samples. Variations in sodium (Na^{+}), potassium (K^{+}), chloride (Cl^{-}) and nitrate(NO_3^{2-}) were investigated in selected samples.

For field sampling, acid-washed, high-density polythene screw-top bottles, of 250 ml capacity, were used, for their practical advantages of being virtually unbreakable and light in weight. Bottles were completely filled, to minimise any gas exchange with air, which could particularly affect species in the carbonate equilibria.

Nitrate measurements were performed (if at all) prior to sample pre-storage treatments, as were EDTA titrations for Ca^{2+} and Mg^{2+} when possible (otherwise extra buffer solution was added to compensate for acidification), and also any laboratory cross-checks of field measurements.

Samples were generally filtered within 8 hours of collection, to minimise changes in chemical equilibria between solutes and sediments (after ALLEN, 1974), and never longer than 32 hours after collection. In the latter case, intermediate storage took place at 4-6°C.

A Whatman glass fibre filter, with retention pore size 1.6 µm (ref. GF/A) was normally used. 'Blank' solutions were filtered and stored in the same manner as the sample solutions, to investigate any contamination on filtering, or leaching of ions into solution from the bottle walls, during storage. Filtered solutions were decanted into 125 ml polythene bottles with screw tops and no inner rubber ring on the cap seal, since this was considered to be a source of serious contamination (R.L.F. Kay, pers. comm. 1981). Acidification of samples to pH2 took place using 2.5 ml 1M HCl, to reduce the risk of precipitation of metal cations during storage (MACKERETH et al.,1978) and to suppress biological activity. Hydrochloric was preferred to nitric acid for its safer transportation in concentrated form, to field laboratories. Treated bottles were stored in normal room conditions.

The untreated samples, stored for stable isotope (oxygen and hydrogen) measurement were used for chloride analysis.

3.3.3 Soil water and cave drips

The sites chosen for the interception of soil moisture and cave drips in the two areas have been presented in section 3.2. Sampling techniques for these waters were chosen to be:-

(1) inexpensive to install;

(2) non-destructive;

(3) not significantly altering flow paths within the immediate area of the sampler;

(4) easy to maintain on a schedule of monthly visits only.

Details of the methods of moisture extraction and drip collection are given below. In section 3.5 is an experimental comparison of different

moisture extraction methods, giving an assessment, in isotopic terms, of the method routinely employed.

3.3.3(a) Soil moisture collection

Samples of soil moisture were obtained using a modified tensiometer system, similar to the suction lysimeters described by WAGNER (1962, 1965) and by PARIZEK & LANE (1970). Such devices have been examined by LEVIN & JACKSON (1977) in a comparisons of *in situ* extractors for sampling soil waters, and were found to be suitable for regular field sampling.

A simple design of suction sampler was chosen in preference to a more sophisticated model, as for example developed by STEVENSON (1978), the latter being designed for the collection of large water samples for chemical analysis (typical sample volumes, 250-500 ml). Since sample volumes as small as 10 ml are acceptable for stable isotope analyses, the model illustrated in fig. 3.20 was considered suitable. A sampler installed in the Lambourn area is shown in plate XIII.

The suction samplers were made by the author, using the shafts and cups of tensiometers extracted from sites previously monitored by the Institute of Hydrology. Prior to installation, the completed samplers were individually tested for free water uptake, suction being applied while the porous pot was submerged in a measuring cylinder of water. The results of the tests (Turf Hill samplers only) are given in table 3.8. Behaviour of the samplers was found to be variable, but generally free-water entry under vacuum provided sufficient sample after approximately half an hour, whereas entry was slight when no vacuum was applied.

For installation, a hole was augered to a prescribed depth, using a Jarrett auger of exactly the same diameter as that of the suction sampler (O.D. 2.3 cm), and the hole base moulded by gentle tamping with a steel attachment replica of the porous pot. A slurry of coarsely-sieved soil from the sampling depth was poured back down the hole, to ensure good contact between pot and soil (P. Stevens, written pers. comm. 1981).

Complete protection of the samplers against grazing livestock was difficult to achieve, fencing off of the area on Turf Hill not being practicable. Several different methods were tried. Unprotected samplers, although projecting 5 cm or less above the ground, were liable to have the polythene tubing chewed by sheep, or else the whole assembly removed by cows. The protection devices tested, of cairns, flowerpot and plastic cover, are illustrated in fig. 3,21 and listed in table 3.8. (The flowerpot protection was used for a suction sampler installed in calcareous drift at High Stables (NGR SD 892674), above Malham Tarn Field Centre; it was not possible, however, to include $\delta^{18}O$ analyses from this site in the present study.) The simple cairns around the sampler were the most successful, being relatively inconspicuous and providing the least danger to livestock. After less than one year, however, soil moisture sampling ended after complete destruction of the samplers in the Malham area, by cattle. There was no grazing livestock at the Lambourn site (Manor Farm), no protection provided and no interruption of the sampling programme.

The following procedures were employed for the extraction of soil moisture, with reference to fig. 3.20. Initial suction was applied using a MitYvac hand vacuum pump (manufactured by Neward Enterprises, California), attached to tube A (clib B closed). Clip A was closed after evacuation, and the applied suction recorded on the MitYvac dial was normally in the range $8.1\text{-}8.5 \times 10^4$ Pa. The sampler was left and after a prescribed time, the sample collected.

On return, the approximate residual vacuum was recorded via tube A. Using the exhaust nozzle of the pump, air pressure was then exerted on the sample collected which, with clip B open, was expelled from the sampler via tube B into a fresh 30 ml glass bottle set inside a measuring beaker and the collected volume measured ($\pm$ 1 ml).

Samples were taken on a monthly basis, but with each monthly sampling, a second sample over a period of between 20 minutes and 2 hours was taken, to be representative of the soil moisture present on the day of sampling.

A trade-off is recognised in the sampler's cheapness and ease of maintenance, against problems of determining the representativeness of soil moisture collected by this method. At initial levels of suction at 8.5×10^4 Pa (or 0.85 bar), some rapidly available capillary water will be extracted from the soil (BRADY, 1974), but as the suction falls below 7×10^3 Pa (0.07 bar) with intake of sample, only gravitational water will enter the sampler. The extent to which exchange and/or reverse flow of the moisture sample may occur in an extended sampling period was considered by STEVENSON (1978) but cannot be quantified for the design of sampler used in this study.

If, in future studies, stable isotopes are used specifically to investigate detailed mechanisms of water movement in the unsaturated zone, more intensive instrumentation would certainly be required, both for sample collection and for description of the soil water flow nets (as, for example, examined by ATKINSON, 1978).

3.3.3(b) Cave drip collection

Cave drips were collected in Chapel Cave, and derived from a near vertical fissure described in section 3.2.1(e). A simple arrangement of a 15 cm diameter funnel leading into a 2 litre (plate XIV) or a 5 litre (fig. 3.22) polythene container was used to collect the drips. Silicone fluid (~30 ml) in the container prevented re-evaporation of the stored sample, although in the reduced temperature range of the high humidity cave environment, such effects were expected to be small.

Using this rather temporary equipment, problems were encountered of (a) obtaining no sample due to inaccurate positioning of the funnel and/or flow path diversions in different flow regimes, and (b) overflow from the container in wet periods, as also experienced by GOEDE et al. (1982). A more permanent

structure, such as used in GB cave by FRIEDRICH (1981), might have been more appropriate, using a larger capacity container, and retaining the silicone oil layer, in consideration of the larger area of exposure of stored sample. Alternatively, a large polythene bag with no air space, for example, as used in the collection of blood for transfusion, could be tested for future studies.

30 ml samples were decanted from the cave drips collected on a monthly basis, as performed for the decanting of precipitation (section 3.3.1(a)).

3.4 Laboratory analyses

Both isotope and chemical analyses are included in this section.

Analysis of the sampled waters for the stable isotopes of oxygen and hydrogen is central to this thesis. Most effort was invested in $^{18}O/^{16}O$ measurements, due to the relative reliability and ease of measurement of multiple samples and for the comparison with other hydrological studies which had similarly concentrated upon the oxygen isotopes. D/H measurements were made on selected samples, and particularly where evaporative effects were suspected, to test for variations in the $\delta^{18}O$-δD slope.

3.4.1 Isotope analysis

Analysis of the natural waters for the stable isotopes of oxygen, hydrogen and carbon were all undertaken by the author in the Isotope Measurements Laboratory, AERE Harwell. Measurements of radioactive tritium were provided by the same laboratory.

Stable isotopes of oxygen ($^{18}O/^{16}O$)

The oxygen isotope composition of water samples was determined by equilibration with $CO_{2(g)}$, and subsequent measurement of the isotopic ratio of the CO_2 gas, according to the classic method of EPSTEIN & MAYEDA (1953), described more recently by ROETHER (1970) and by GONFIANTINI (1981).

A diagram of the preparation line is shown in fig. 3.23. Into each clean

50 ml flask was introduced 5 ml of water sample, using a glass pipette (laboratory grade 'A', with accuracy $\pm$ 0.015 ml at 20°C). The laboratory working standard of East Hendred borehole water was used as an internal standard for each batch, in flask positions H_1 and H_2 (fig. 3.23).

With the flask taps closed, the water was frozen by immersion of the flasks in a freezing solution of acetone and solid carbon dioxide (temperature approximately -78°C), and air evacuated from the flasks, lowering the pressure to approximately 20 Pa. Care was taken not to pump above any liquid water, since this would cause kinetic isotopic frationation. The ice was then melted by immersion of the flasks in a bath of water (at $\sim$20°C), and the freezing down and evacuation processes repeated, to ensure complete removal of non-condensable gases from the flasks. Commercial cylinder carbon dioxide of known isotopic composition was then introduced into the preparation line, from the 2 litre reservoir (vacuum pumps sealed off) to a pressure of approximately 9.6×10^4 Pa. After an allowance of 10 minutes for the CO_2 gas to achieve (isotopic) homogeneity throughout the preparation line, the flasks were individually sealed and transferred to a water-bath at 25.0 $\pm$ 0.1°C. Isotopic exchange takes place between $CO_{2(g)}$ and water according to the reaction:

$$C^{16}O_2 + H_2{}^{18}O \rightleftarrows C^{16}O^{18}O + H_2{}^{16}O$$

via CO_2 in the aqueous phase forming the hydrogen carbonate ion plus protium in its reaction with water (GONFIANTINI, 1981) viz:-

$$CO_{2(g)} \rightleftarrows CO_{2(aq)}$$

and $$CO_{2(aq)} + H_2O \rightleftarrows HCO_3^- + H^+$$

Equilibration was encouraged by the (mechanical) shaking of samples in the

water-bath. After a minimum of 10 hours, samples were individually taken from the water-bath and the equilibrated CO_2 gas passed through a cold trap, shown in fig. 3.24, to obtain a moisture-free $CO_{2(g)}$ sample, at approximately 4.0 10^4 Pa, for isotopic measurement by mass spectrometry. A timed 10 minutes was allowed for this transfer and drying process.

Using a high-precision, light element mass spectrometer, the sample CO_2 ratios of mass 46 ($^{12}C^{18}O^{16}O$, $^{13}C^{17}O^{16}O$, $^{12}C^{17}O_2$) to masses 44 ($^{12}C^{16}O_2$) and 45 ($^{13}C^{16}O_2$, $^{12}C^{17}O^{16}O$) were measured with respect to a reference CO_2 gas of known isotopic composition. Within each batch of 10 samples, isotopic ratios of the 8 unknown waters were referred to the international isotopic standard, SMOW, through the average measured ratios of the 2 internal standard waters, to derive $\delta^{18}O_{SMOW}$ in units of $^{o}/oo$ (per mil). The basic principles and operation of the mass spectrometer, together with details of the standardised (delta) calculation are given in Appendix A.

Instrumental precision of measurement by mass spectrometry, for individual CO_2 samples, with respect to the reference gas, was better than $\pm$ 0.04 $^{o}/oo$ (at 1σ) from a total of 12 ratio measurements. Estimation of the total reproducibility of a particular $\delta^{18}O_{SMOW}$ value, however, is dependent upon the many additive errors of volumetric measurement, and minor variations in fractionation factors, due, for example, to temperature variations in the freezing mixture or water bath. Within-batch precision of measurement from preparation of 10 East Hendred borehole water samples was found to be 0.06 $^{o}/oo$ (at 1σ). Estimation of an individual sample's reproducibility, over the long term, with comparison between batches, was obtained by examination of the reproducibility of $\delta^{18}O_{SMOW}$ of the internal standards. For n=210 (105 batches, 2 samples in each batch, from 10.12.80 to 30.3.83), an overall precision (at 1σ) of 0.10 $^{o}/oo$ was found, and this is comparable with precisions declared by other laboratories, for example, at the IAEA Isotope Laboratory (GONFIANTINI, 1981, p.80). It is noted, however, that the estimate

of error presented here does not refer to the whole isotopic range of waters (cf. GONFIANTINI, op cit.), nor does it include variations due to the effects on fractionation of water chemistry variations between samples. For the small range of non-saline waters examined, however, it is anticipated that this source would add negligible error to the declared analytical error.

The absolute accuracy, and hence intercomparability of $\delta^{18}O_{SMOW}$ measurements has been assessed by laboratory measurements of the international water standards provided for this purpose, viz. SLAP, SMOW and GISP. The results of measurements, performed by the author, show the system of standards used in the Harwell Laboratory to be quite satisfactory for intercomparisons.

Stable isotopes of hydrogen (D/H)

The hydrogen isotopic composition of water samples was determined by mass spectrometric analysis after quantitative reduction of the water, over uranium, to hydrogen gas. The preparation method using uranium as a reducer was first reported by BIGELEISEN et al. (1952), but the first accurate hydrogen isotope analyses of natural waters were made by FRIEDMAN (1953).

The preparation line used at the Isotope Measurements Laboratory is shown in fig. 3.25. Using a glass capillary pipette (Dade Capilets Microhematocrit Tubes, reference B4415.10), approximately 2-5µl was introduced into the inlet finger (cf. 10 µl used by DARLING & BATH, 1979). The water was then frozen in the finger, using liquid nitrogen (temperature approximately -196°C), and non-condensable gases were pumped off. This was essential since the introduction of any nitrogen over hot uranium would form a coating of uranium nitride and inhibit the reduction process. A hot tape was then applied to the finger, at approximately 200°C, to evaporate the water sample. With taps B and D closed, the vapour was allowed to enter the furnace which contained turnings of fresh depleted metallic uranium, heated to 850°C.

The following reaction with the hot uranium took place:-

$$2H_2O_{(g)} + U_{(s)} \rightarrow UO_{2(s)} + 2H_{(g)}$$

The evolution of hydrogen gas was indicated by a rise in pressure at Pirani gauge 1 (background pressure of 2.7 Pa), rising to off-scale, i.e. greater than 27 Pa, with hydrogen production. Only one pass over the uranium was required, and negligible amounts of non-reduced water were recorded in the liquid nitrogen trap.

Powdered metallic uranium was used to collect the hydrogen gas produced, a technique demonstrated by FRIEDMAN & HARDCASTLE (1970) as an alternative to the use of a Toepler pump. The uranium powder was first exposed, at approximately 650°C, to the hydrogen gas, with taps B and E closed. The external heating coil was then switched off, and the following reaction took place, at about 80°C:-

$$2U_{(s)} + 3H_{2(g)} \rightarrow 2UH_{3(s)}$$

The reaction was judged to be complete when the vacuum indicated by gauge 1 had returned to the initial (background) level. This took between 12 and 25 minutes, depending upon the purity of the powdered uranium. (Note that the presence of gases other than hydrogen would prevent a complete return to background pressures.) The heating coil was then switched on again, with taps C, D and F closed. With heating to 650°C, the uranium hydride was quantitatively decomposed to release hydrogen, which was collected in the (pre-evacuated) sample flask, over a period of 8 minutes.

The first gas produced after warm-up of the apparatus was unreliable and always rejected; the second water prepared was a sample of the international standard, SMOW. One sample of SMOW was included in the preparation for every five water samples of unknown isotopic composition. The heated powdered uranium was pumped over between samples, to minimise any memory effects.

The isotopic composition of the hydrogen gas was measured using the VG Isogas 602E mass spectrometer, and Appendix A describes its operating principles and the method of δD_{SMOW} calculation.

Instrumental precision (at 1σ) for an individual ratio was better than $\pm$0.25 $^{o}/_{oo}$. An investigation of the long-term reproducibility of the internal standard, SMOW, gave an estimate of reproducibility of $\pm$1.3 $^{o}/_{oo}$ (at 1σ for n=36). This may be compared with the declared long-term reproducibility of other laboratories eg. of 0.8 $^{o}/_{oo}$ of the IAEA Isotope Hydrology Laboratory (GONFIANTINI, 1981).

The absolute accuracy, and hence inter-comparability of δD_{SMOW} measurements was assessed by the measurement of the international standard waters, and results were satisfactory.

Stable isotopes of carbon ($^{13}C/^{12}C$)

Carbon dioxide gas was obtained, for mass spectrometric analysis, by the acidification of the dried strontium carbonate samples (section 3.3.2(c)). Concentrated ortho-phosphoric acid (H_3PO_4) was used, as recommended by McCREA (1950). It has a low vapour pressure and is therefore suitable for use in vacuum systems, and the fractionation factor associated with its use for carbonate acidification is known. It also has a low activity of water in its concentrated solutions, and therefore a low probable exchange rate between oxygen in the solution and the gaseous CO_2 produced (McCREA, op. cit.).

Approximately 95% phosphoric acid was prepared from 85% phosphoric acid, by the addition of phosphorous pentoxide ($\sim$50 g to 1 litre of acid) on heating the acid to approximately 200°C. Complete removal of water from the acid was not considered desirable (cf. A.H. Bath unpublished MS, recommending the further additions of chromium trioxide and hydrogen peroxide) since the increased viscosity makes the acid more difficult to handle. Comparisons of results using 100% phosphoric acid in a series of experiments on selected carbonates were, however, in excellent agreement, with those using the 95% acid.

The strontium carbonate sample was powdered (section 3.3.2(c)) to provide a maximum surface area for the reaction, and 0.2 g (± 10%) was weighed out and placed in the acidification vessel of the preparation line, shown in fig. 3.26. The vessel was evacuated and tap A closed. 15 ml of acid was gradually added to the carbonate powder, and carbon dioxide gas was immediately released.

The mixture was agitated, using a magnetic stirrer, and after 10 minutes, the pre-evacuated line was opened up to tap C, further promoting the production of CO_2. The process was allowed to continue for a further 20 minutes, by which time visible gas production was normally negligible, although the reactant solution was never clear (probably due to the insolubility of $SrHPO_4$). The pressure of gas produced in the line varied between 2.7 and 4.0 x 10^4 Pa.

The flask of dry CO_2 sample was transferred to the mass spectrometer, and measurement made of the mass 45/44 ratio and the mass 46/(44 + 45) ratio. Operational details and the method of calculation of $\delta^{13}C_{PDB}$ are given in Appendix A.

Instrumental precision on an individual ratio measurement was normally better than ±0.03 ‰ (at 1σ, 45/46 ratio). A sample of precipitate from a 20 litre batch of laboratory tap water was included in sample batches as a cross check on preparation and instrumental stability. Reproducibility of these samples on the same day was good, ±0.09 ‰ (1σ, n=9). For this same internal standard, from 15 measurements (from 10.2.82 to 17.6.82), a precision of ±0.23 ‰ (at 1σ) was found, using consistently the method of preparation described above.

Accuracy, hence intercomparability, of the $\delta^{13}C_{PDB}$ results was ensured by the calibration of the CO_2 gas, in use as a machine reference on the mass spectrometer, against gases prepared from a suite of international standards

(including carbonates requiring acidification), carried out by the Harwell Laboratory.

Tritium (^3H)

Tritium levels in water samples were measured by staff of the Isotope Measurements Laboratory, according to the methods of electrolysis and gas proportional counting described by ALLEN et al. (1966).

There is no reference standard for tritium measurements, since results are presented in terms of ^3H concentrations by direct measurement, converting measured activities into absolute concentrations (calculated for the day of sampling). The overall accuracy of a single measurement is normally ± 2 TU or 5%, whichever is the greater (OTLET, 1977, p.1).

3.4.2 Analysis of water chemistry

In this section will be given a summary of the analytical procedures used for each chemical species examined.

All of the analyses except for 50 major cation determinations were made by the author. Others were performed by staff of the School of Geography, Oxford.

Calcium and magnesium

Both methods of complexiметric EDTA titration and atomic absorption spectrophotmetry were used in Ca^{2+} and Mg^{2+} determinations.

When sample preservation and transportation was problematic, but basic laboratory facilities available, as at the Malham Tarn Field Centre (and particularly with hydrograph sampling), titrations were undertaken. Analysis took place normally within 4 hours or sampling, but occasionally, with the use of the automatic sampler, up to 10 hours after sampling.

BDH water hardness kits were used in titrations for total hardness and calcium hardness, magnesium hardness being the difference between the two. The procedures of DOUGLAS (1968; pp.12-14) were followed. Using the average of two sample titrations, minus a repeated 'blank' reading (using distilled

water), absolute measurements of Ca^{2+} were liable to an error of $\pm$1.1 ppm $CaCO_3$ ($\pm$0.4 ppm Ca^{2+}). An additive error of $\pm$2.3 ppm was attributed to Mg^{2+} determinations. Levels of iron (eg. 0.040 ppm), aluminium (eg. 0.300 ppm), manganese (eg. 0.005 ppm), barium (eg. 0.04 ppm) and strontium (eg. 0.06 ppm) were sufficiently low in the types of water studied to assume negligible interference in EDTA titrations. The ionic levels given as examples above were measured in selected stream samples from the Malham area, using the Institute of Hydrology Plasma Emission spectrophotometer. Unfortunately, comparable data were not available for the Lambourn area, but no difficulties in the recognition of the end points, nor abnormally high hardness results, which might have been attributable to such interference (DOUGLAS, 1968), were noted.

The original intention in this study had been to measure calcium and magnesium concentrations using atomic absorption spectrophotometry, the principles of which may be found elsewhere (for example, in GOLTERMAN et al. 1978). Unfortunately, from September 1981, it became evident that the spectrophotometer (Pye Unicam model SP191) at the School of Geography, Oxford, had electronic faults and was becoming increasingly unstable. An example of repeat measurements made at this time is shown in fig. 3.27. Prior to this, the accuracy of measurement was at best $\pm$1 ppm Ca^{2+} (for concentrations of less than 100 ppm) or $\pm$5 ppm Ca^{2+} (for concentrations greater than 100 ppm), and $\pm$0.6 ppm Mg^{2+}, the error being substantial in calcium determinations due to the large dilution factors required. A buffer solution of 10 000 ppm K^+ and 4% $LaCl_3$ was added to both sample and standard solutions to control possible interference from Si, Al or P and to suppress ionisation, as recommended by COOK & MILES (1980).

Atomic absorption spectrophotometer facilities (Perkin-Elmer 603) were made available at the Institute of Hydrology in October 1982, and analysis for Ca^{2+} and Mg^{2+} with increased precision was possible. Estimates of

reproducibility were ±0.5 ppm Ca^{2+} and ±0.02 ppm Mg^{2+} (for concentrations 0-1 ppm) or ±0.10 ppm Mg^{2+} (for concentrations 1-4 ppm), including the errors introduced by acidification and dilution.

No significant additions of calcium or magnesium (detection limits 0.1 ppm and 0.005 ppm respectively) were found in bottles of blank solutions which had undergone preservation (acidification) treatment and had been stored for four months prior to analysis (at the Institute of Hydrology), thereby eliminating a possible source of positive error in these ion concentrations.

Although measurements of magnesium were complete, further reporting of this species is excluded, due to its strong co-variance with calcium determinations. The latter are reported, in preference, due to their higher levels, at which experimental error is of less significance.

Other ionic species

Occasional measurements on selected samples were made of the following ionic species, using the standard techniques specified:-

(1) Sodium and potassium determinations by flame emission photometry (method of GOLTERMAN et al., 1978).

(2) Chloride determinations, by Technicon Autoanalyser, based on standard spectrophotometry (method of COOK & MILES, 1980).

(3) Nitrate determinations, by nitrate selective electrode (method of EDWARDS et al., 1975).

These measurements are excluded from reporting, however, due to the lack of complete and reliable data sets, a factor which arose due to emphasis upon the need for isotopic characterisation of the water.

3.5 Experimental investigations into stable isotope sampling methods

Four investigations into stable isotope sampling methods are presented in this section. Each has important bearings on the reliability of results to be reported in Part 4, and each makes a contribution to stable isotope hydrology by providing certain recommendations for future sampling methods.

Investigations into the collection of precipitation follow on from the discussions concerning theoretical aspects of precipitation collection in section 3.3.1(a). Results are analysed from the long-term monitoring of monthly precipitation, with and without the use of oil, and at sites which offer different exposures. The remainder of experimental investigations were performed in the laboratory. They were initiated to ensure that the methods employed of water storage, snow melting and soil moisture extraction would each provide satisfactory and reliable results.

3.5.1 Storage of water samples

This laboratory experiment examined the isotopic effects of five different combinations of water storage conditions. The aim of the experiment was to assess the effectiveness of an oil film in suppressing evaporation, and to investigate possible isotopic changes in samples stored in the two bottle types most frequently used in this project.

Water samples of the same initial isotopic composition were subjected to five different combinations of storage conditions. These were:-

(1) 30 ml water in closed 30 ml capacity glass bottle, no oil (method of routine long-term storage for stable isotopes, in this study)

(2) 500 ml water in closed 1.3 litre capacity polythene bottle, no oil (method of routine interim storage for weekly precipitation samples)

(3) 500 ml water in open 1.3 litre capacity polythene bottle, with oil film (replicating water stored in raingauge receiver with oil)

(4) 500 ml water in open 1.3 litre capacity polythene bottle, no oil (for comparison with (3))

(5) 20 ml water in open 30 ml capacity glass bottle, no oil (for comparison with (1)).

Results of δD analyses of the samples, up to 370 days after initiation of

the study, are shown in fig. 3.28. Evaporative enrichment of the open container samples, (4) and (5), clearly occurred. After 10 days, the 500 ml open sample was isotopically enriched by 16 $^{o}/_{oo}$, but no enrichment was detectable in the corresponding sample under oil. After 82 days, however, a small degree of enrichment was apparent in the latter sample, probably caused by disturbance of the oil film and dispersion of the film, possibly enhanced by dust accumulation on its surface. Evaporation clearly continued towards the end of the experiment, and a total enrichment of 78 $^{o}/_{oo}$ is observed. The isotopic deviations through time of the closed 30 ml and 500 ml samples, however, do not exceed measurement error.

We may conclude that the oil film appears to act as an effective suppressant of evaporation even in extreme laboratory conditions, provided that the film is not broken. Care should therefore be taken to ensure that the film is clean and continuous. The 30 ml glass bottle routinely used in this study, and the 1.3 litre polythene bottle used for interim storage, when closed, both appear satisfactory for storage of water without detectable isotopic modification. Results using these bottles for storage may therefore be considered reliable.

3.5.2 Collection of precipitation

The prinicipal aim of this investigation was to determine whether the use of an oil film, for the suppression of evaporation in precipitation collection, was necessary in the temperate maritime climate of the U.K. A variety of precipitation collectors were chosen for use in the investigation (table 3.6, section 3.3.1(a)) to compare also the performance of standard and non-standard styles for stable isotope studies.

Results of isotope analyses were first examined for monthly precipitation collected in 'paired' raingauges at sites where collection was made both without and with the use of an oil film. The discrepancies between collections are shown in table 3.9. The $\delta^{18}O$ difference was calculated as;-

$$\text{Difference } (^{o}/_{oo}) = \delta^{18}O \text{ (no oil)} - \delta^{18}O \text{ (oil)}$$

eg. for Warren Down Farm data, May 1982:-

$$\text{Difference} = -5.1 - (-5.4)$$

$$= +0.3\ ^{o}/_{oo}$$

If significant evaporation were taking place within the 'no oil' raingauge, isotopic enrichment would result, which would be recorded as a positive difference in $\delta^{18}O$. From theoretical considerations of open system evaporation presented in section 2.2.5(d), we would expect such a difference to vary directly with soil temperature and inversely with relative humidity and with precipitation amount. The latter effect is explained by a constant evaporation rate producing a greater impact upon the relative fraction, f, of liquid evaporated if the initial amount of liquid is small.

The observed $\delta^{18}O$ differences, however, in table 3.9 are both positive and negative and fall in the range +5.8 to $-0.8^{o}/_{oo}$, although 91% of differences are within 1 $^{o}/_{oo}$ of 0.0. A negative difference cannot be explained by an evaporative effect. A significant difference is one greater than 0.2 $^{o}/_{oo}$ (at 1σ measurement error); this value is exceeded in 33% of all cases. The observed isotopic differences do not appear to reflect the strongly seasonal patterns of relative humidity (minima in May/June/July, fig. 3.29(a) and (b)) or of soil temperatures (maxima in July/August, fig. 3.29(c) and (d)). Neither is a clear relationship found with precipitation amounts (which are presented in Part 4).

The correlation coefficients, r, between the isotopic difference and the meteorological parameters named above, using a least-squares linear regression, fall in the range -0.44 to +0.79 (table 3.10). The coefficients vary greatly between sites, corresponding with the great variations in isotopic difference between sites. This may reflect the differences in style

and collector used. The only correlation coefficient which is significant at the 95% level of confidence (2-tailed test), in the direction anticipated, is that between the isotopic difference and monthly mean earth temperature at Warren Down Farm ($r=0.59$, $n=12$). This is the only location where a Snowdon style collector, with a wide-mouthed inner receiving bottle, was used for 'no oil' collection. In view of enrichment in summer of the 'no oil' sample, it is suggested that this style may be unsuitable for reliable precipitation sampling for stable isotope analysis in the U.K.

The smallest absolute isotope differences are seen at Malham Tarn Field Centre and the largest at Lechlade. Rainfall collectors at the former site are perhaps the most reliable (Snowdon style with oil; Bradford style without); at the latter site, the 'Harwell' collector was used and this factor, in addition to peculiarities of siting of the collectors will be discussed later.

High correlations between the isotope difference and meteorological variables at Malham Village, in a counter-intuitive direction (r values being positive with relative humidity, negative with temperature and positive with amount) are difficult to explain. The data set available is small (n=13 or 14) and correlations must be strongly dependent upon anomalies in particular months, for example upon the negative difference in July 1982.

It is possible that exchange may occur of oxygen isotopes in the water with those in atmospheric CO_2, in a process similar to that utilised in the $\delta^{18}O$ equilibration preparation method (section 3.4.1). If oil prevented this exchange, an inverse relationship of the isotopic difference ('no oil' minus 'oil') with temperature would be expected, according to the variations of per mil enrichment (expressed as $10^3 \ell n \alpha$)with temperature (fig.2.4). However no consistent evidence of such a process is found in these results, probably due to the relatively low partial pressure of CO_2 in the atmosphere.

Both evaporative alteration on storage and isotopic exchange with CO_2 are negated by examination of the $\delta^{18}O$-δD plot in fig. 3.30, which shows no consistent shift, positive or negative, in $\delta^{18}O$, for the paired oil/no oil data of the Malham area. This is exemplified by the most severe shifts of January 1982 and January 1983 which are each in opposite directions. There is no evidence for a lowering of the $\delta^{18}O$-δD slope away from a regression line describing collection under oil.

A possible explanation of certain isotope differences lies in the field observation of condensation droplets on upper internal surfaces of certain gauges. If considered as closed system evaporation under high relative humidities, this phenomenon may have resulted in small, but detectable, isotopic fractionation (GILATH & GONFIANTINI, 1983). Particular care was taken to ensure inclusion of such droplets by complete mixing prior to emptying the raingauge, but this was not supervised at Lechlade (collected by AERE staff), and was not practicable at Warren Down Farm, where a Snowdon collector was used with no oil, and not an 'enclosed' Bradford or Octapent collector, as used elsewhere. The testing of this possible source of error requires a separate experiment.

Finally, it is suggested that the observed $\delta^{18}O$ differences ('no oil' minus 'oil') might be, at least in part, attributable to differences in actual catch of paired rainfall collectors, over the sampling period. It has been shown, for example, by SHARON (1972) that the standard error of catch for adjacent collectors (in a dense network) may not be reducible beyond 4%, due to the 'spottiness' of precipitation itself, and this may be reflected in isotope results.

Differences in volumetric catch between paired collectors are difficult to assess exactly, because the presence of oil, on decanting the precipitation, may cause over estimation, or equally over compensation, in a volumetric measurement, thereby increasing the normal error bar of $\pm$ 1 mm (5"

funnel). Figure 3.31(b) illustrates, however, the normally good agreement in catch at Malham Tarn Field Centre using the Snowdon and Bradford style raingauges, catches being referred to the monthly total sum of daily rainfall measurements. Comparisons of catches elsewhere are shown in figs. 3.31(a), (c) and (d). The good exposure of the rainfall collectors and similarity of style appear to be important factors improving the comparability of catch, as might be expected (eg. from RODDA, 1969). These factors are optimised in the Malham area and at Warren Down Farm. Lechlade was considered to have a poor exposure, the stable isotope sampling site being only 2 m away from a 2 m conifer hedge, which was aligned NW-SE. This was likely to be the cause of locally high variations in catch, due to its influence on the aerodynamics of rain-carrying wind as, for example, found near shelter belts (GEIGER, 1965). Indeed, the agreement in catch of the Octapent style (no oil) raingauge at Lechlade with the nearby (recommended exposure) daily reporting Meteorological Office raingauge was found to be exceptionally poor (fig. 3.31(d)), with correlation coefficient, r, of 0.38 (n=14). In addition, collections at Lechlade were made under oil using the Harwell style collector. The catch of this non-standard gauge, from comparisons between styles at Malham Tarn Field Centre, was found to be erratic, both in volume, and in $\delta^{18}O$ recorded, as shown in fig. 3.31(b) and table 3.9, respectively.

It is suggested that variations in volumetric catch may reflect discrimination between rainfall types (eg. according to their associated intensity, direction of prevailing wind and windspeed) and therefore produce isotopic differences between precipitation samples collected. The variable catch by raingauges of blowing or drifting snow is perhaps the most obvious source of isotopic variation. Variations in catch could equally occur in drizzle or driving rain. Further analyses and experimentation would be required, however, to quantify such effects.

It is concluded from the isotopic differences presented that

reproducibilty of precipitation collection appears to be strongly dependent upon exposure, and, to a lesser extent, precipitation collector type. Where these factors are optimised, reproducibility of paired samples appears to be almost equal to the isotope measurement precision.

Wherever possible, rainfall values referred to will be those collected under oil in Meteorological Office approved collectors. The lack of oil in the Fountains Fell raingauge, however, is not considered to be critical because (a) it has a good exposure (Meteorological Office approved), (b) any evaporation effects at this coolest and wettest location are expected to be minimal, and (c) the Octapent design allows for the re-inclusion of condensation droplets in the sample, as thorough mixing of the sample is facilitated in the inner can.

As a general guideline, the continued use of the oil or silicone fluid layer is recommended in the U.K. except where a Bradford or Octapent style collector may be used, and particular attention is drawn to consideration of exposure whenever a collector is sited for sampling.

3.5.3 The melt of snow samples

The melt of fresh snow samples, for inclusion in weekly precipitation samples, was specified at the outset of this study to take place in an enclosed container (section 3.3.1(a)). It was unknown, however, how sensitive the isotopic result may be to the method of snow melt employed. A meteorological observer might normally melt over a stove any snow trapped in a raingauge funnel at the time of an observation. An experiment was designed to test the method of snow sample melt in a sealed container (30 ml glass bottle) as compared with more rapid melting of the snow, indoors, in an open container.

A sample of snow, weighing approximately 1.3. kg, from the site of AERE Harwell on 13.1.1982, was divided between four large (1.25 litre) Pyrex crystallising bowls (samples 1-4) and one small (500 ml) dish (sample 5).

Samples 1 and 2 were melted on an electric hob, sample 1 on a hotter ring than sample 2. Samples 3, 4 and 5 were allowed to melt on the laboratory bench. Laboratory air temperature was approximately 18°C, and relative humidity was estimated to be 40-50%. Samples of water for isotopic measurement were taken when complete melt of the snow had occurred. The dishes were left open after complete melt, on the laboratory bench, and a further sample taken after 3 days. In this time sample 5 evaporated to dryness. A sample of the original snow was also packed into a 30 ml glass bottle which was tightly sealed, and the snow allowed to melt.

$\delta^{18}O$ results of the experiment (fig. 3.32) show a tendency of the snowmelt in open containers to be isotopically light compared with the sealed melt sample, on initial slow melting (samples 3,4,5), with a difference in the range of -0.7 to -1.6 °/oo. This may be attributed to the condensation of isotopically light water vapour onto the melting snow/ice itself, and onto the cool container walls, a phenomenon which was observed during the experiment. Heating on the electric hob produced isotopic enrichment, which was initially enhanced in sample 1 with strong heating, but initially not apparent in sample 2, probably counterbalanced by condensation effects.

After 125 minutes, with approximately 7% loss of water mass due to heating (fig. 3.33), samples 1 and 2 were both enriched by approximately 1.1 °/oo, relative to the sealed snowmelt sample. After 4140 minutes, an isotopic enrichment of the order of 11.4 to 16.8 °/oo had developed, associated with between 40 and 60% cumulative losses by evaporation of samples 1 and 2 respectively.

In view of the isotopic deviations which may result from open container melt, the sealed bottle method is recommended as the most suitable and simple for the sampling of snow for isotopic analysis.

3.5.4 Soil moisture extraction

The method of soil moisture extraction by suction cup samplers was chosen

for this study primarily because it fulfilled the four practical requirements listed in section 3.3.3(a). The possible dependence of isotopic results on the extraction method used, however, were unknown.

A small number of experiments were therefore undertaken to evaluate different methods of soil moisture extraction. The techniques investigated were:-

(1) In situ extraction by suction cup samplers

(2) Centrifuge extraction from soil samples, by drainage

(3) Centrifuge extraction from soil samples, by displacement

(4) Vacuum distillation of water from samples.

Technique (1) was employed for routine sampling and is described in section 3.3.3(a). Centrifuge extraction by drainage, shown in fig. 3.34(a), followed the method of EDMUNDS & BATH (1976), designed for the removal of interstitial waters from porous rock cores. This was found to be most suitable for peaty soils, but drainage from soils with high clay content was prevented by compaction on centrifuging. The alternative method of extraction (method (3)), by displacement of soil moisture by Arklone P® (a fluorinated hydrocarbon, manufactured by ICI) was then employed, as developed and recommended by D. Kinnenborough (pers. comm., 1981), and illustrated in fig. 3.34(b) and (c). Water so extracted with centrifuging was pipetted from the surface of the Arklone, with which it is immiscible. This method was found to be unsuitable for soils with high humus content, since the latter floated above the Arklone and interfered with moisture sample recovery. For both centrifuging methods (2) and (3), spinning was at high speed (at 4600 or 13000 rpm for 45 minutes), and at a constant temperature ($10^{o}C$).

A fourth method of extraction, by vacuum distillation, followed the methods used in the Isotope Measurments Laboratory for the extraction from rock cores of moisture for tritium analysis. Soil samples were placed in a sealed oven heated to $105^{o}C$. Water vapour produced was drawn by vacuum into a

series of three liquid nitrogen traps (at -196°C). When drying was complete, the extracted moisture collected in the traps was melted and combined as one sample.

Stable isotope results of the soil moisture samples extracted are given in table 3.11. It is observed that isotope results from centrifuge extractions of A and B_s horizons (using methods (3) and (2)) appear to be similar at the chosen sampling times (viz. Knowe Fell samples: 7.6.1981, 28.6.1981, 4.9.1981). With the exception of peat from Manor Farm water meadow (2.7.1981), water extracted by the suction cup method was found to be isotopically lighter than that extracted by the other methods.

The isotopic differences between vacuum distillation and displacement are seen to be only slight and indicate little isotopic difference in the additional water extracted by the distillation method.

The major difference between method (1) and the other methods is in the level of suction which is applied and therefore level of soil moisture tension which is overcome in extracting the moisture. Suction cups are effective only to soil moisture tensions of 1.0×10^5 Pa whereas vacuum distillation at 105°C extracts all water to approximately 31.4×10^5 Pa (CURTIS & TRUDGILL, 1974) (Note that 1.013×10^5 Pa is equal to 1 bar, and approximates normal atmospheric pressure). Intermediate suction values of between 6.9×10^5 Pa, (at 13000 rpm) and 2.4×10^5 Pa, (at 4600 rpm) are effective in centrifuging. The slower centrifuge speeds of samples taken after 27.6.1981 are reflected in the lower gravimetric yields relative to total moisture content, a value which is maximised by the vacuum distillation method.

From this discussion of soil moisture tensions, the isotopically heavier results in samples (2)-(4), (table 3.11) indicate that the more tightly held water (at > 1 bar) is itself isotopically heavier. This may be explained by the satisfaction of soil moisture deficits, after summer drying of the soil, by isotopically heavy waters(late summer isotopically enriched precipitation

and/or evaporative enrichment of recharging water). These may be tightly retained, with more mobile water contributing to the fluctuations observed in the 2.4 to 6.9 x 10^5 Pa methods of extraction. An alternative hypothesis is that selective retention, ie. a fractionation process, is occurring in the soil, possibly by diffusion processes similar to those discussed by FOSTER & SMITH-CARRINGTON (1980) for tritium in recharge waters. Exact determination of the mechanism and its hydrological implications (eg. in terms of isotopic evidence for by-pass pipe flow in peat soils) requires controlled laboratory experimentation. Initial studies, for example, by JUSSERAND (1980), have shown that even in controlled conditions, isotopic behaviour in soil moisture uptake may be extremely complex. Where concern is focused on the processes of mobile water transmission, however, it would appear sufficient to examine soil moisture extracted at the lower tension (method (1)), and suction cup extraction is therefore confirmed as a suitable method for this study.

PART 4 RESULTS AND DISCUSSION

4.1 Introduction

In Part 4 will be presented the results of isotope analyses and conventional hydrological measurements, at both the monthly and within-storm timescales of sampling. Waters will be divided into four categories which will be discussed in turn. These are: precipitation, monthly samples of surface and groundwater, soil moisture and cave drips and finally storm samples of surface water from the Malham area. The first two categories constitute the most fundamental part of this study and will receive the greatest attention. The main isotopic results will be presented in the introduction to each category. General observations will be made concerning the major features of the measured isotope signals, before ancillary results are presented. A more detailed analysis and discussion of the results will then follow in each section. Summary details of the statistical routines employed may be found in Appendix B.

4.2 Isotopic input signals in precipitation

The results of $\delta^{18}O$ analyses of monthly precipitation are given for each of the collection sites: Fountains Fell (fig. 4.1), Malham Tarn Field Centre (fig. 4.2), Malham Village (fig. 4.3), Lechlade (fig. 4.4) and Warren Down Farm (fig. 4.5). A feature of all these results is that an isotope input signal is obtained which is clearly definable. The total range of $\delta^{18}O$ values observed is from approximately -3 to -13 $^{o}/_{oo}$, representing one hundred times current measurement error ($\pm$ 0.1 $^{o}/_{oo}$ at 1σ).

This is an important observation since, to a large extent, the application of the stable isotope technique is determined by the definition of the input signal in precipitation. A similarity in the isotope pattern at the three Malham area sites is discernable, although no altitude effect is immediately evident. The isotope signals in general, however, do not appear

to be strongly seasonal, presenting a more erratic pattern than might be expected from a summation of the climatological isotope 'effects'.

An even more erratic isotope signal is seen in weekly precipitation at Malham Tarn Field Centre (fig. 4.6 and 4.7). A wider range of $\delta^{18}O$ values, from -17.3 to -2.7 $^{o}/oo$, is revealed in weekly sampling which remain unobserved in the corresponding monthly values. The relationship of the signal with meteorological parameters is unclear, but demands further investigation if the input signal is to be fully exploited for the purpose of natural tracing. Still further complexity of the isotopic input pattern is apparent in within-storm collection of precipitation; examination of these results is reserved until the end of this section.

First, the detailed nature of the isotope signals in monthly and weekly precipitation collections and the implications for their use in hydrological studies in the U.K. will be examined.

4.2.1 Monthly precipitation

4.2.1(a) Results

Monthly $\delta^{18}O$ signals in precipitation, measured at each of the five principal collection sites, are presented in figs. 4.1 to 4.5 and also in tables 4.1, 4.2 and 4.3, together with monthly meteorolgical parameters. These parameters, where available, include total precipitation, mean monthly temperature, and effective precipitation. Results of δD analyses will be discussed, in section 4.2.1(b). Except for Fountains Fell, the monthly data refer to precipitation collected under oil. Shading of the months November-April on the horizontal axes of isotope plots indicates the position of the 'winter' season.

Monthly precipitation totals at Lechlade for the months November and December 1982 were not available, and data have been used from the nearest comparable Meteorological Office raingauge at Kempsford (NGR SU 148972), which is 7.8 km WSW of Lechlade, and 7 m higher at 79 m O.D.

It has been found that, in most cases, monthly $\delta^{18}O$ values match to within ± 0.2 °/oo the sum of weekly $\delta^{18}O$ values, weighted for relative precipitation amounts. This difference corresponds to 2 standard deviations in measurement precision, and therefore we have confidence at the 95.4% level (2-tailed test) that there is no significant difference between the two measured values. A fair comparison is limited, however, by the number of times an exact correspondence of sampling dates, and therefore of precipitation totals, occurred (viz. April '81, June '81, July '81, August '81, March '82 and July '82 at Malham Tarn Field Centre). This limited cross-check does, however, provide some confidence of internal consistency in the sampling techniques employed.

4.2.1(b) The $\delta^{18}O$-δD relationship in monthly precipitation

Figs 4.8 and 3.30 plot the $\delta^{18}O$-δD relationship in monthly precipitation at Fountains Fell (FF) and at Malham Tarn Field Centre/Malham Village (M), respectively. Least-squares linear regression analysis of the two data sets provided the following results (table 4.4):-

(a) $\delta D_{FF} = (7.28 \pm 0.30)\delta^{18}O_{FF} + (4.45 \pm 2.20)$

(b) $\delta D_{M} = (7.22 \pm 0.51)\delta^{18}O_{M} + (3.10 \pm 3.85)$

The correlation coefficients are high: r=0.98 (n=24) and r=0.95 (n=23), respectively. The slopes of the regression lines are in good agreement with each other, despite differences in collection procedure (section 3.5.2), and are slightly lower than that of CRAIG's (1961a) Meteoric Water Line (MWL, slope = 8), although the difference at Malham Tarn Field Centre/Malham Village is only significant at the 75% level (table 4.4). A high standard error is associated with the estimates of the intercept parameter but in both cases these are lower than that of the MWL, ie. 10; significant differences from this value are found at the 95% and 90% levels for the FF and M data sets respectively. This is discussed in detail later in this section.

Similar regression coefficients (although without expression of standard

error) for precipitation elsewhere in the U.K. have been reported since this study was first undertaken. These include those of BATH et al. (1984):-

$$\delta D = 7.89\delta^{18}O + 8.82$$

for weekly rainfall collections in Cambridgeshire, 1979-1983, using a reduced major axis regression. THORPE (1981) found the following relationships:-

$$\delta D = 7.11\,\delta^{18}O + 3.05$$

at Lechlade, Oxfordshire, for monthly precipitation (1978-1980), and

$$\delta D = 7.20\delta^{18}O + 5.61$$

in the Malham area for combined stream water and precipitation monthly samples (1978-1980).

The use by BATH et al. (1984) of the reduced major axis method allows for the choice of independent/dependent variable to be ignored, and is applicable since the analytical errors in the isotopic data are proportionally comparable to the variations of $\delta^{18}O$ and δD (YURSEVER & GAT, 1981). Where correlation between the mean values of $\delta^{18}O$ and δD is very strong, however, (as has been shown above), both methods produce similar results, and the linear least-squares method was preferred in this study for comparability with published IAEA results.

EVANS et al. (1979) calculated a relationship for precipitation over 'maritime Europe', from 6 IAEA/WMO Precipitation Network stations, to be:-

$$\delta D = 6.9\delta^{18}O - 0.3$$

The relationships actually observed in the present study are intermediate between that of the most 'maritime' Valentia to the west (for which $\delta D = 6.77\ \delta^{18}O - 4.61$ for 1957-1978) and stations to the east of the U.K. (eg. Gröningen, Netherlands, for which $\delta D = 7.54\delta^{18}O + 8.44$ for 1964-1978). (IAEA, 1981b).

The observed slope close to 8 indicates net equilibrium conditions of vapour distillation. The downward shift in the intercept in comparison with the MWL is interpreted as indicating a source of vapour where kinetic

evaporation effects are minor (point V_{n-e} lying close to point V_e, and residual line E being little changed from that of L in previous fig. 2.16).

The calculated mean d-excess parameters (previously defined in equation 2.18) are 10.1 °/oo for Fountains Fell data, and 9.4 °/oo for Malham Tarn Field Centre/Malham Village data, which are both close to the value of 10 °/oo specified for the Meteoric Water Line. The values have been calculated over two complete annual cycles (Jan. 1981-Dec. 1982 inclusive), with data gaps filled using corresponding isotope values from within the Malham area. If the same monthly d-excess values are weighted for total monthly precipitation amounts, respective parameters of 10.6 °/oo and 9.7 °/oo are obtained. Weighting for effective precipitation gives d-excess values of 11.3 and 10.3 °/oo; this weighted value is the one which may be expected to be found in currently recharging waters, mixed over a period of 1 year or more, if no isotopic modification of the recharge occurs.

It is interesting to note the seasonal variation of d-excess, illustrated in fig. 4.9, which brings about the observed shift in the mean d-excess value when weighting is applied. A high d-excess is generally found in winter, often close to or exceeding the MWL value, and a lower value is found in summer. In certain winter months where heavy snowfalls are reported, it appears that the d-excess may also be low (eg. in January/February 1981/1982 at Fountains Fell, and also in January 1983). The cyclical d-excess pattern suggests either a seasonally variable source of water vapour or else control of isotopic concentrations by seasonal patterns in condensation, or even post-condensational re-evaporation. The latter process would tend to produce a slope in the $\delta^{18}O$-δD plot of less than 8 (DANSGAARD, 1964), but since the d-excess simply expresses the position of a point relative to the MWL, the exact nature of the shift is obscured. A significant correlation at the 95% level with relative humidity, however, (fig. 3.29(b)) of d-excess in the Fountains Fell data set ($r=0.60$, $n=24$) indicates that such a mechanism may be

operational; relative humidity was found experimentally by STEWART (1975) to be a strong controlling factor of evaporation from raindrops. A direct causal link cannot be reasonably proposed, however, without more detailed isotopic data, for example, of in-cloud water vapour over the U.K.

As a second stage of analysis of the seasonal patterns observed in the $\delta^{18}O$-δD relationship, months of precipitation were divided into the seasons of winter and summer, for which the months of November-April and May-October inclusive were chosen, as plotted by symbols in fig. 4.8 for the Fountains Fell data. Re-analysis of this data set gave the following least-squares regression relationships:

Winter

$$\delta D = (7.54 \pm 0.43)\delta^{18}O + (6.96 \pm 3.36) \quad ; \quad n=14$$

Summer

$$\delta D = (7.28 \pm 0.43)\delta^{18}O + (3.73 \pm 2.98) \quad ; \quad n=11$$

A lower slope and/or intercept value was intuitively expected of the summer data relative to the winter data, but no significant differences are found between the parameters, nor between those of the main data set and the seasonally-divided sets (table 4.4). It is suggested, therefore, that the seasonal isotopic characterisation, using this method, is inadequate, in this area, to be of use for natural tracing studies.

4.2.1(c) Seasonality in monthly precipitation

The total range in $\delta^{18}O$ of 10 $^{o}/_{oo}$ in monthly precipitation samples has previously been noted (section 4.2.1(a)). The variability of the input signal is important because its strength defines its potential for use in stable isotope natural tracing studies, as compared worldwide in section 2.3.2(d).

The variance (σ^2) of monthly isotopic values in precipitation may be used to express the variability or seasonality of isotopic input at a site. Values of this index, together with related summary statistics, are presented in two tables. Table 4.5 gives data summaries for standardised periods of full

annual cycles (12 or 24 months), with data gaps filled by correlation with adjacent collection stations, as indicated. Table 4.6 summarises all observations made at the precipitation collection stations, and data gaps are not filled. For an optimum comparison with published records the former table will be used; in many cases, it is evident that data from table 4.6 are comparable, but the computed means tend to be isotopically lighter (for example, in a comparison of $\delta^{18}O$ means at Malham Tarn Field Centre), due to the inclusion of additional winter months, in more than 2 years of sampling.

The values of monthly isotopic variance (σ^2) are lower for the here reported U.K. stations than those generally found in more continental climates (category III, table 2.6), or in the dry or periodically dry climates (category IV), by a whole order of magnitude (eg. for $\delta^{18}O$, σ^2 of 2.2 at Fountains Fell, as compared with 18.2 $(^{o}/oo)^2$ in Vienna). The $\delta^{18}O$-δD slope of $\sim$8 excludes the observations from categories IV and V, and marginally greater variances are observed in the U.K. stations than in those listed as island/ship locations (category I). The coastal station grouping of category II is the most appropriate. Variances observed are comparable to those in Valentia, and the mean weighted d-excess parameters similar, although tending to be higher than that of 7.4 reported for Valentia. THORPE (1981) suspected evaporation from the collecting raingauge at Valentia to be the cause of an unusually low slope here (unweighted value, 6.77), but it is considered here that this may be the product of initial non-equilibrium rainout of saturated air masses first passing over land, over south-western Eire. The finer divisions by STRAHLER's (1969) climatic type in table 2.7 provide an additional placing in context of the U.K. data. Of the examples here, the isotopic variability in the U.K. data is exceptionally low. This matches the comparative lack of monthly temperature variability in the marine west coast category (7), the data for Valentia here probably representing the lowest variability, and the U.K. falling intermediate between this and temperature variability on mainland NW Europe.

The U.K. precipitation data may be considered in the context of the previous figs. 2.18 and 2.19 (from YURTSEVER & GAT, 1981), which show the relationships of $\delta^{18}O$ variability with weighted mean $\delta^{18}O$ and with temperature variance, respectively. In fig. 2.18, data from this study plot as an island station, intermediate between Valentia and Port Stanley (Falkland Is.). A continental station having approximately the same weighted $\delta^{18}O$ mean as Fountains Fell (eg. Flagstaff, Colorado Plateau, U.S.A., mean $\sim$-7.6 $^{o}/oo$) may experience a standard deviation of isotopic input over three times larger than that observed in the U.K. (5.1 $^{o}/oo$ as compared with 1.5 $^{o}/oo$). In fig. 2.19, it is evident that the U.K. data plot near the median of reported worldwide values in terms of monthly temperature variance, but their disproportionately low variance in $\delta^{18}O$ places the data again among island stations (lower subgroup of set A).

The seasonality of signal observed in figs. 4.1 to 4.5 is clearly much less emphasised or regular than that, for example of Vienna, illustrated in fig. 2.20 (from YURTSEVER & GAT, 1981; note the inverted isotope scale).

Isotopic variations in the Malham area in particular appear erratic from month to month. The degree of first order smoothing in a time series may be expressed by its autocorrelation coefficient at a lag of 1, expressed as r_1, the correlation coefficient of $\delta^{18}O_t$ with $\delta^{18}O_{t-1}$ (DAVIS, 1973). This value is much higher for a smooth signal such as that of Vienna, for which r_1 is approximately 0.50 (YURTSEVER, 1975), than for the Malham area, where values range from -0.3 (Fountains Fell data) to 0.25 (Malham Tarn Field Centre). This procedure of autocorrelation of a time series may be extended to lag L, and figs. 4.10 and 4.11 show the Malham and Lambourn area $\delta^{18}O$ precipitation data in the form of correlograms, plotting r_L against L. Lags are shown only up to 14 months, which represents approximately n/2 of the full data sets. For statistically sound interpretation of the r_L values, a relatively long

series is required (eg. n=50), and a maximum lag of n/4 is recommended by DAVIS (1973), due to the loss of data incurred in lagging one series against itself which produces instability in the lagged correlation coefficients. Interpretation of the computed correlograms presented is therefore cautious.

Minor peaks of positive correlation are found in each correlogram at the 11 month lag. Over a longer sampling period it is possible that this may actually converge on the lag of 12, indicating the annual periodicity. The agreement of the 11 month period between the correlograms suggests a common driving mechanism over the sampling period investigated. The roughness of the correlograms, however, indicates a large amount of 'noise' in the series. From such short time series, it is probable that individual events are strongly reflected in the correlograms. An example is the isotopically light precipitation of September 1981 and the isotopically heavy precipitation of April 1982 at Fountains Fell, which contributed strongly to the peak negative value of r_L at lag 7 months.

The Warren Down Farm $\delta^{18}O$ signal in precipitation (fig. 4.5) is smooth in comparison with the Malham data (autocorrelation at lag 1, 0.32), exhibiting more regularly the anticipated pattern of isotopically heavier input in the summer, and isotopically lighter input in the winter. It is notable that the ranges of isotopic variation in the two areas are comparable, from -10.6 to -4.4 $^{o}/_{oo}$ in the Lambourn area, and from -9.8 to -3.6 $^{o}/_{oo}$ in the Malham area, if the extreme value at Malham Village for December 1981 is omitted.(This value was possibly caused by drifting and melt of snow in the lower altitude raingauge). Correlogram analysis is severely limited in the short Warren Down Farm series, for which n=12. A strongly inverse autocorrelation coefficient at lag 6 months, however (fig. 4.11(b)), indicates the relatively emphatic annual periodicity at this site.

The complexity of the $\delta^{18}O$ signal in the Malham area, compared with that at Warren Down Farm, may be due to the very variable influence of relief in NW Yorkshire, on passing weather systems, which may have a complicated history

of isotopic development according to the exact trajectories of local air mass movements.

All the U.K. correlograms are however more erratic than that shown in fig. 4.12(a) for Vienna. In fact, a greater resemblance is found with the Vienna correlogram in which the annual periodicity has been removed (fig. 4.12(b)).

4.2.1(d) The altitude effect (Malham area)

In the Malham area, it was possible to examine the isotopic altitude effect on $\delta^{18}O$ on a monthly basis over a range of 472 m. A visual comparison of figs. 4.1 to 4.3 reveals a similarity of $\delta^{18}O$ patterns in precipitation at the three stations; computed correlation coefficients in terms of both $\delta^{18}O$ and precipitation amounts are all significant at the 99% level of confidence, as shown in the correlation matrix of table 4.7. This is despite slight variations in sampling intervals between Malham Tarn Field Centre/Malham Village (co-synchronous with surface water sampling) and Fountains Fell (sampling on the first of each calendar month, except where access was prohibited by adverse mountain weather conditions).

Fig. 4.13 plots three combinations of differences between the monthly $\delta^{18}O$ values. A significant difference in measurements is one greater than 0.2 $^{o}/_{oo}$. An erratic pattern of altitudinal differences is seen. Table 4.8 presents the range of altitudinal isotope effects which might be anticipated in this area under various combinations of lapse rate and associated isobaric/adiabatic cooling, using data from TAYLOR (1976) and SIEGENTHALER & MATHER (1981). The isotopic gradient with moist adiabatic cooling is expected to be the most relevant for comparisons of monthly data within a small geographical area. For the Pennine region this may give a gradient for $\delta^{18}O$ of -0.26 $^{o}/_{oo}$ /100 m which is close to the mean value of possible isotopic gradients calculated. All values are negative: only a temperature inversion would produce a positive gradient, by this method of theoretical estimation.

In fig. 4.13, both positive and negative differences are actually observed in the Malham area. A negative difference indicates that isotopically lighter precipitation is being collected at a higher altitude. Isotopic enrichment is in fact most common from Malham Tarn Field Centre to Fountains Fell (class (a)). This may be due to (1) a bias in isotope collection at Fountains Fell, (2) a bias in collection at Malham Tarn Field Centre, and/or (3) a true reversal of isotopic gradient. Confidence has been expressed in the style of raingauges used as collectors in the Malham area (section 3.5.2). The Malham Tarn Field Centre station is, however, the least well exposed of the three, and this has caused concern in records of temperature (MANLEY, 1957) as well as precipitation amount. Since the completion of this study, the station at the Field Centre has actually been moved, after recommendations by the Yorkshire Water Authority, from its previous site on the lawn of Malham Tarn House, to a more exposed site some 10 m away, on the northern bank of the Tarn. It is notable that the mean isotopic depletion with altitude is greatest from Malham Village to Malham Tarn Field Centre (mean -0.34 $^{o}/_{oo}$ over 210 m). From the bottom of the study area to the top (class (c)) a positive mean gradient of 0.05 $^{o}/_{oo}$ (σ=1.18) is recorded, shown in table 4.9.

It is possible that a smooth gradient of isotopic input with altitude is not to be expected in this area, at monthly or even at shorter intervals . Modification by relief of local circulation patterns may allow precipitation in Malham Dale (oriented approximately N-S) to be derived from air masses with significantly different trajectories, and therefore different isotopic histories, from those precipitating over the Fells to the North. Very dynamic depression systems might tend to totally mix the isotopic input which may become uniform over an area and range of altitudes. The atmospheric conditions which would most promote the altitudinal isotope effect are the relatively stationary systems, with orographic rainfall triggered in warm,

moist and therefore unstable air. Such conditions are most likely in the summer in the U.K.

Re-examination of fig. 4.13 shows the isotopic depletion to be more common in summer. By division of the year into winter and summer months (as indicated on the sampling scale bar and presented in table 4.9), a mean total summer altitude effect of -0.11 $\pm$ 0.13 $^{o}/oo$/100 m was calculated for all three classes, and a mean total effect of -0.50 $\pm$ 0.39 $^{o}/oo$/472 m for the Malham Village-Fountains Fell data set. This effect is smaller than any of those summarised in table 4.8 (range -2.0 to -0.9 $^{o}/oo$/472 m). The observed winter effect is more variable and positive (eg. 0.46 $\pm$ 1.41 $^{o}/oo$/472 m). Weighting of the monthly isotopic differences for precipitation amount has a variable effect on the isotope gradient. The greatest depletion effect is, however, the unweighted mean of summer data in class (b) of -0.54 $^{o}/oo$/210 m (σ=0.33), i.e. -0.26 $^{o}/oo$/100 m, which corresponds in table 4.8 with the depletion calculated for moist adiabatic cooling in the Pennines (using the lapse rate data of MANLEY, 1943). Extrapolating the 'optimum' effect in Malham, the maximum U.K. range of 1345 m (section 1.1) would give an isotopic difference of only 2.6 $^{o}/oo$, assuming the altitudinal effects measured in NW Yorkshire to be representative of upland U.K. conditions.

In conclusion, the observed altitude effects are in general slight and unpredictable, and even the 'optimum' effect unlikely to be of practical applicability in the U.K. There is an advantage in the lack of an altitude effect, however. Since the isotopic input exhibits only small and approaching random spatial variations, it may reasonably be assumed to be uniform over the study area, at the monthly timescale. This greatly simplifies considerations of ground and surface water input-output responses.

4.2.1(e) Temperature and amount effects

The temperature effect discussed by DANSGAARD (1964), for which an empirical relationship was described for maritime North Atlantic stations

(fig. 2.12), referred to mean annual isotope concentrations in precipitation. If mean annual temperature values, for stations Malham Tarn Field Centre and Warren Down Farm (6.8°C and 8.8°C, from table 4.5) are substituted into equ. 2.16, the respective estimates of mean $\delta^{18}O$ in precipitation obtained are -8.9 and -7.6 °/oo. The predicted value for Malham is isotopically lighter than the observed mean weighted $\delta^{18}O$ value (-8.0 °/oo), whereas the predicted Berkshire value is isotopically heavier than that observed (cf. -7.8 °/oo). Observed values may come closer to predicted long-term averages with longer periods of sampling. Data are too limited to suggest that a more gentle isotopic gradient of 0.2 °/oo/2°C (ie. 0.1 °/oo/°C, cf ∿0.7 °/oo/°C) is generally observable in the U.K. A larger number of representative stations with long term observations would be required to follow up this study.

The remainder of this section will consider the month-to-month isotopic variations with respect to possible temperature and amount effects.

Figures 4.2 and 4.5 show both temperature and precipitation data for the meteorological observation stations at Malham Tarn Field Centre and Warren Down Farm, respectively. There appears to be an underlying seasonal trend in $\delta^{18}O$ values (examined in section 4.2.1(c)), but a trend which exhibits significant variations between possible lines joining the peaks and troughs, in $\delta^{18}O$ values especially as compared with the smooth, strongly seasonal pattern of temperature variations.

In general, isotopically light precipitation is seen to occur in months of low mean temperature (eg. December), and isotopically heavy precipitation in warmer months (eg. July), as is expected. In addition, specific examples may be seen of isotopic enrichment being associated with small precipitation amounts (eg. May 1982, Warren Down Farm; October 1982, Malham Tarn Field Centre), and isotopic depletion with large precipitation amounts (eg. March 1982, Warren Down Farm; March 1981, Malham Tarn Field Centre).

Regression analyses were performed to quantify the isotope 'effects' in

precipitation, with a view to their application in hydrological studies. The independent variables considered were:-

(1) Monthly arithmetic mean temperature, MATEMP, derived from daily values for each sampling period;

(2) Monthly mean temperature derived from daily temperatures, each weighted according to daily precipitation amounts (MPTEMP);

(3) Monthly mean temperature derived from daily temperatures, each weighted according to daily effective precipitation amounts (MEPTEMP);

(4) Total monthly precipitation amount (MPPT);

(5) Total monthly effective precipitation amount (MEPPT).

Values of all the independent variables were available at Malham Tarn Field Centre and at Warren Down Farm. Elsewhere, only regressions of $\delta^{18}O$ in precipitation with MATEMP and MPPT were performed.

Results of the least-squares linear regression analysis are presented in table 4.10. Although many of the relationships are statistically significant at the 95% level and above, levels of explained variance are in many cases rather low. This apparent discrepancy arises from the strong linearity of the relationships, accompanied by considerable scatter about the regression. Scatter plots in figs. 4.14 (Malham Tarn Field Centre data and 4.15 (Lambourn area data) illustrate this point.

It is interesting to examine the sign and strength of the regression coefficients, summarised in table 4.10, to assess the potential to predict isotopic concentration where only meteorological data are available, and vice versa.

All relationships of monthly $\delta^{18}O$ with MATEMPT are significant at the 95% level, and this includes cases where temperature data is used from distant meteorolgical stations (eg. Lechlade using Warren Down Farm data). The slopes of the regression range from 0.13 (Malham Village) to 0.26 (Fountains

Fell), these particular values apparently indicating greater sensitivity to temperature of $\delta^{18}O$ in precipitation at a higher altitude than in a valley location. The regressions found at Malham Tarn Field Centre (MTFC) and Warren Down Farm (WF) respectively are:-

$$\delta^{18}O_{MTFC} = (-8.87 \pm 0.39) + (0.18 \pm 0.05)\ MATEMP_{MTFC}$$

and

$$\delta^{18}O_{WF} = (-9.25 \pm 0.81) + (0.22 \pm 0.08)\ MATEMP_{WF}$$

The positive slope is in agreement with the theoretical temperature effect discussed by DANSGAARD (1964), but is less steep, than that found for a group of four 'representative' stations in the northern hemisphere of the IAEA/WMO sampling network by YURTSEVER & GAT (1981), viz.:-

$$\delta^{18}O = (-14.96 \pm 0.21) + (0.521 \pm 0.001)MATEMP$$

n=363, r=0.89

The subdued sensitivity to temperature measured in this study reflects the maritime lack of strong temperature variations, and possibly the dominance of the other processes causing $\delta^{18}O$ variations in the U.K. The observed levels of explanation of variance, from 18 to 44% are, however, up to twice as high as those found in Valentia (IAEA, 1981b), where only 17% of $\delta^{18}O$ variations are explained by monthly mean temperature.

Mean air temperatures have been widely used in quantification of the 'temperature effect', and the good relationships found elsewhere have been explained by either the parallel variation of (surface) temperatures with upper air (ie. condensational) temperatures, and/or by the dependence of post-condensational processes on the air temperature (section 2.3.2(b)). MPTEMP was introduced as a variable which would be more meaningful in physical

terms than MATEMP, aiming to represent air temperatures at the time of precipitation. The improvement is limited, however, by the use of an average daily temperature, (½[daily max. + min. temperature]). In fact, a near 1:1 linear relationship is found between arithmetic mean and precipitation weighted temperatures, as shown in the scatter plot of fig. 4.16 for weekly values. Only a slight improvement of explanation is found by inclusion of MPTEMP at MTFC (explained variance of 37% as opposed to 34% using MATEMP), and a reduction in explained variance is actually found at WF. Slope and intercept values change little with the use of MATEMP, MPTEMP or MEPTEMP (correlations with the latter are poor at WF), with slopes of 0.18, 0.21 and 0.21 respectively at MTFC. The hydrological implications of these observations are that interpretation of $\delta^{18}O$, in recharging waters, with respect to temperatures at the time of precipitation may make use of a single sensitivity factor to temperature, at the monthly scale. The sensitivity at this timescale is much smaller than that reported by DANSGAARD (1964) of ~0.7 $^{o}/_{oo}/^{o}C$ which refers to mean annual temperatures. SIEGENTHALER & MATHER (1983) expect a suite of lower slope $\delta^{18}O$-temperature relationships to cross the DANSGAARD general relationship, monthly values reflecting the moist adiabatic temperature dependence (see table 4.8) as opposed to the stronger isobaric cooling effect which controls mean annual $\delta^{18}O$ variations through space.

Turning to the amount effect, correlations of monthly $\delta^{18}O$ with precipitation amount (MPPT) are all found to be negative; all are significant at the 95% level, except for those at Malham Village and at Lechlade where the relationship is weak (the latter shown in fig. 4.15). The slope of relationships elsewhere range from -0.036 to -0.006, the 'amount effect' gradient being slightest on Fountains Fell. The two meteorological stations give results:-

$$\delta^{18}O_{MTFC} = (-6.01 \pm 0.44) + (-0.012 \pm 0.003)MPPT_{MTFC}$$

and

$$\delta^{18}O_{WF} = (-4.72 \pm 0.80) + (-0.036 \pm 0.010)MPPT_{WF}$$

Explanation levels are higher here than for the 'temperature effect'. The slope of the line at MTFC is comparable with that of Valentia (-0.01 ± 0.00; IAEA, 1981b) and also the equatorial island stations (slope, -0.015, fig. 2.13). The steep slope of WF, however, is close to those of stations exhibiting a monthly amount effect which dominates the isotopic input signal, eg. Windhoek, S. Africa, slope -0.05 ± 0.01 (n=123, r=0.59). Little change is observed by the use of effective precipitation in correlations using U.K. data.

An improved correlation is obtained by the inclusion of both the temperature and precipitation amount in a multiple linear regression (table 4.10). By convention, a positive value for r, the correlation coefficient, is given for the case of multiple linear regression.

Fortunately, the two meteorological variables are not themselves highly correlated, and therefore problems of multicollinearity are expected to be small (FERGUSON, 1977). Correlation coefficients between MATEMP and MPPT are -0.20 and -0.21 at MTFC and WF respectively (n=27, n=12). The best explanation (83% of variance) is found at WF, using MATEMP and MPPT in a linear regression. The corresponding regression at MTFC yields an explanation level of 64%. Using MPTEMP instead of MATEMP at MTFC, the explanation inceases to 67%, which is the highest level found in the Malham area.

4.2.1(f) Assessment of the monthly isotope input as a tracer for hydrological applications

Smoothing of the input signal over a period of one year or more, for example in slow moving and well mixed groundwaters, would be expected to produce isotope values close to the mean of input values in precipitation. It is the

isotopic deviations from such a mean value weighted for precipitation amount which are most likely to be of use in natural tracing studies, since they provide the clearest signal of a recent input water.

The following means (of full annual cycle data sets) are included in table 4.5:-

A. Arithmetic mean of monthly $\delta^{18}O$ values in precipitation

B. Mean of monthly $\delta^{18}O$ values, weighted for the total precipitation in each month

C. Mean of monthly $\delta^{18}O$ values, weighted for the effective precipitation in each month (using Malham Tarn Field Centre and Warren Down Farm daily values for the appropriate sampling intervals in the respective areas).

A general pattern is noted of means A >B> C. This reflects the larger quantities of isotopically light winter precipitation which contribute to total precipitation amounts, and also to effective recharge. Isotopically heavier precipitation receives progressively reduced weighting in the calculation of A, B and C.

Considering mean B, a water derived from precipitation mixed over 1 year or more may be expected to have a $\delta^{18}O$ value between -8.0 and -7.6 $^{o}/_{oo}$ in the Malham area, approximately -7.8 $^{o}/_{oo}$ in the Lambourn area, and approximately -8.3 $^{o}/_{oo}$ around Lechlade. This assumes that (a) the sampling of isotopic input is reliable (least likely at Lechlade, as already discussed), and (b) that no evaporation, removal or isotopic modification occurs of the recharging water. If mean values C are proposed, we assume that there is total evaporation of non-effective precipitation or total retention/uptake of water contributing to a soil moisture deficit, and again that there is no isotopic modification of the effective precipitation water prior to recharge.

It is interesting to note that the mean δD precipitation values A, B, C for the Malham area, if the $\delta^{18}O$ values are translated by the $\delta^{18}O$-δD

relationship computed for MTFC data (table 4.4), lie in the range of groundwater δD values mapped over the U.K. by SONNTAG et al. (1983) in a pattern depicting the whole of NW Europe. δD means A, B, C of -52, -55 and -57 $^{o}/oo$ are obtained, respectively. Using the same equation for Lambourn (WF) data, means -50, -53 and -60 are obtained. These are actually lighter than the groundwater values predicted for the Berkshire area (-40 to -50 $^{o}/oo$), although direct comparisons of the published figures with measured precipitation averages are limited by our inability to reduce to sea level the averages, when observed altitude effects are erratic over the U.K.

Observed means A and B are heavier in the South of England, which is generally warmer than the North. Mean C, however, is lighter in the Lambourn than in the Malham area. This may reflect the impact of greater evapotranspiration of summer precipitation in the specified Lambourn catchment, as compared with the upland Malham area (land use types being used in the calculation of effective precipitation were defined for each area in tables 3.2 and 3.4). It will be interesting to note whether a direct correspondence with any of the means computed is found in the groundwaters of the study areas, in an assessment of current recharge processes using the stable isotope technique (section 4.3.2).

In conclusion, an isotopic signal which is definable well beyond measurement error, and which is therefore available for natural tracing studies, has been identified at the monthly scale in the U.K. For the precipitation sampled, up to 55% of $\delta^{18}O$ variation may be explained by a single meteorological variable, and up to 83% by a combination of meteorological variables. Exact prediction of monthly $\delta^{18}O$, however, requires high levels of explanation and therefore it seems unlikely that reliable estimates of isotopic input could be made for hydrological studies in the U.K., at this timescale, without concomitant isotopic monitoring.

This is in contrast, perhaps, with areas which exhibit a more reliable,

strongly seasonal pattern of input, eg. continental Vienna, where extrapolation of input signals, in order to examine an output value, is more well-founded. It seems unlikely that a future increase in the ability to predict, say, mean monthly temperature and precipitation, would improve the precision of prediction of $\delta^{18}O$ in the U.K.; such prediction is a desirable objective since it would enable improved planning in the timing of tracing studies. Extreme events within the month appear to dominate the patterns of the isotopic signals. It is possible that, with the highly variable pattern of weather in the U.K., correspondence of monthly $\delta^{18}O$ and climatic parameters is reduced due to the grouping at this timescale of the causal meteorological variables. At a finer level of resolution, weekly and within-storm isotope patterns will be examined in sections 4.2.2 and 4.2.3 respectively.

In addition, the appropriateness of the timescale chosen for natural tracing studies evidently depends upon the input-output response of the hydrological system under investigation. Weekly or shorter period sampling may be more suitable in 'fast' systems, and therefore such isotope signals require examination.

4.2.2 Weekly precipitation

4.2.2(a) Results

Results of $\delta^{18}O$ measurements from weekly precipitation samples collected at Malham Tarn Field Centre over a two year period (January 1981-February 1983) are presented in figs. 4.6 and 4.7, together with weekly values of total precipitation and the weekly arithmetic mean of daily air temperatures. A limited number of $\delta^{18}O$ measurements of weekly precipitation were made on samples collected at Lechlade, from the Meteorological Office daily reporting gauge, and these are presented in fig. 4.17, which also shows measured precipitation amounts. Numerical results for the two collection sites are listed in tables 4.11 and 4.12 respectively.

Preliminary measurements of surface waters had shown the Malham area to

be more isotopically responsive than the Lambourn catchment, as had been expected, and therefore it was considered most valuable to concentrate effort in measurement of shorter collection period samples from the former site. The limitations of time in this project allowed only for the measurement of $\delta^{18}O$ in weekly precipitation samples. It is possible that further investigations which include δ D analyses may reveal further interesting patterns by consideration of both isotopic species.

The method of sampling weekly precipitation adopted was found to be satisfactory. Mutual support of the weekly and monthly sampling methods by isotopic agreement of the weighted weekly sum with the corresponding monthly sample, was demonstrated in section 4.2.1(a). Additionally, the experiment to investigate the storage of water in a 1.3 litre polythene bottle, as used for the accumulation of daily rainfall over one week, provided satisfactory results (section 3.5.1). Within the normal storage time before decanting (maximum 6 weeks), negligible isotopic alteration may be assumed to be attributable to the method of storage.

Sample volumes of less than 12 ml (equivalent to 1 mm precipitaton) were, however, rejected from the analysis. Although $\delta^{18}O$ measurement of as little as 1 ml is possible, isotopic alteration was anticipated to be quantitatively much greater in such samples. Seven Malham samples, out of 109, therefore, remained unmeasured, four weeks of which recorded zero precipitation totals. Three out of 25 Lambourn samples were not measured, one week recording zero precipitation.

The results for the Malham data include isotopic measurements of snow which were made separately, and weighted for rainfall equivalence before inclusion in the total weekly $\delta^{18}O$ value. Such weeks are indicated by an asterisk, in figs. 4.6 and 4.7. The technique was not required in the relatively snow-free Lechlade area.

4.2.1(b) Seasonality of $\delta^{18}O$ in weekly precipitation

Figures 4.6 and 4.7 reveal a much wider range of $\delta^{18}O$ values which remain unobserved in the corresponding monthly $\delta^{18}O$ values at Malham Tarn Field Centre (fig. 4.2). The weekly range from -17.3 to -2.1 °/oo compares with the monthly range from -9.8 to -4.8 °/oo, ie. a 200% increase in range at this particular location. A higher standard deviation for weekly values of 2.7 °/oo reflects the wider spread of isotopic input at this timescale, compared with 1.4 °/oo for monthly precipitation. Both these figures refer to full annual periods (January 1981-December 1982, inclusive), and the standard deviations to the samples as populations (ie. n=104, n=24, respectively). Summary statistics shown in table 4.13 show the arithmetic mean of weekly measurements to match that of monthly measurements (ie. -7.6 °/oo,table 4.5). Divergence occurs, however in comparison of weighted means B and C (using the notation of section 4.2.1(f)), for which lighter values are found in weekly data of -8.3 °/oo (total precipitation) and -8.7 °/oo (effective precipitation) respectively. The lack of a match with monthly values may indicate that either (a) a bias occurs in the monthly samples discriminating against isotopically light precipitation, eg. of drifting snow, or (b) small amounts of isotopically heavy precipitation are lost in the transfer procedure of daily precipitation, either being discarded by the observer, or the weekly sum being too small for reliable isotopic measurement. The latter rejection did occur, but for this to be solely responsible for the difference in weighted means, we must assume the small quantities of precipitation involved to be isotopically very significant. It seems more likely that the observed difference results from a combination of the suggested effects.

Although weekly $\delta^{18}O$ values still appear to follow an erratic pattern, superimposed perhaps upon a seasonal trend of peaks and troughs, the calculated serial autocorrelation at lag 1 for this data set is slightly

higher than for the monthly precipitation plots, indicating a smoother series: at L=1, r_L=0.32. Certain patterns of 'steps' are apparent in the weekly $\delta^{18}O$ plots, showing small increases in isotopic concentration, followed by a trough of lighter precipitation. This pattern is most noticeable in the late summer months (July, August, September, October), but is also seen in March 1981 in the plot of weekly $\delta^{18}O$ at Lechlade. Correlogram analysis of the Malham data is shown in fig. 4.18, up to L=54. It is possible that the gentle decline of r_L at short lags is due to the presence of the 'steps', although the small and negative autocorrelation coefficient at lags 6-7, at which the pattern appears to operate, indicates that this is not a dominant feature of the time series. Minor peaks in autocorrelation are found at lags 10-13, 42 and 51 weeks, the latter referring to the overall annual periodicity of the series. Its position at a lag slightly less than one full year is in agreement with the comparable minor peak observed in the monthly precipitation correlograms, and this may be a function of the particular years sampled with respect to the exact timing of atmospheric events. It is probable that the intermediate peaks reflect individual events which are isotopically very significant; an example is the matching of isotopically light winter snowfalls at particular lags in the autocorrelation analysis.

From first principles, the greater variability in weekly isotope values is expected to reflect the greater variability of weekly meteorological parameters. It is possible that at this timescale better explanation of isotope variance may be found because grouping over time of the casual variables will be less severe.

4.2.2(c) Temperature and amount effects in $\delta^{18}O$ of weekly precipitation

Inspection of figs. 4.6 and 4.7 reveals several interesting relationships. The anticipated direct relationship between $\delta^{18}O$ and (arithmetic mean weekly) temperature appears to be strong for particular periods, or runs of weeks. Examples are from late February to the end of

April 1981, December 1981 and early September 1982. Occasions of cold winter spells appear to correlate more dramatically with isotopically light precipitation than warmer periods with isotopically heavier precipitation. At other times, the relationship of the amount effect is seen to operate (ie. low $\delta^{18}O$ with high precipitation amount), eg. in late June 1981, early May and early September 1982, although at the ends of the latter two months a reversal of the expected relationship is seen, ie. $\delta^{18}O$ increases (becomes less negative) with higher precipitation amounts.

It is perhaps more appropriate to consider mean weekly temperatures which have been weighted according to the precipitation amount on a daily basis (WPTEMP), rather than the arithmetic mean of daily values (WATEMP), although the strong, near 1:1 relationship between the means has been noted previously. More scatter in the relationship between WATEMP and WPTEMP is generally observed in winter than in summer, although the outliers noted in fig. 4.16 do not appear to be associated with any particular category of $\delta^{18}O$ values.

Linear regression was carried out between the $\delta^{18}O$ and meteorological variables to investigate the strength and direction of the isotopic effects in weekly precipitation in the U.K.

Results of the linear regressions in table 4.14 show relationships between $\delta^{18}O$ and temperature and precipitation to be significant at the 99% level; confidence in the relationships is enhanced by the high number of samples in the Malham weekly series, in comparison with the corresponding monthly series. In the Lechlade series, however, no relationship is found between $\delta^{18}O$ and precipitation amount. This may reflect isotopic sampling problems at this site, although precipitation was actually collected from a Meteorological Office raingauge, which exhibited a better exposure than the monthly collectors at Lechlade.

The percentages of $\delta^{18}O$ variation explained by the meteorological variables at Malham are, however, lower than those found at the monthly

timescale, eg. 25% of variance explained by weekly average temperatures as opposed to 34% by monthly temperatures. An improvement in the explanation of weekly $\delta^{18}O$ data is found by the use of a multiple linear regression, 34% of variance being explained by WATEMP and WPPT. (Little improvement is found in the use of WPTEMP.)

The direction and strength of the correlation coefficients and partial correlation coefficients at Malham Tarn Field Centre are very similar to those found at the monthly scale although the slopes tend to be steeper, indicating greater sensitivity to meteorological parameters, viz.:-

$$\delta^{18}O = (-9.43 \pm 0.40) + (0.28 \pm 0.05)WATEMP$$

$$\delta^{18}O = (-6.17 \pm 0.40) + (-0.039 \pm 0.009)WPPT$$

Residuals from the multiple linear regression using WATEMP and WPPT as independent variables (table 4.14) are plotted in fig. 4.19, and are seen to exhibit a pattern very similar to that of the original weekly $\delta^{18}O$ series (Malham data). Analysis in section 4.2.2(d) attempts to explain the variation which remains after extraction of the temperature and amount isotopic effects.

4.2.2(d) Air mass considerations of weekly precipitation samples

In view of the rather low correlations found between weekly $\delta^{18}O$ values and weekly temperatures and precipitation amounts, a consideration of the trajectories of precipitating air masses, which are known to be variable over the U.K., and which might be expected strongly to influence isotopic concentrations in precipitation, appeared to be a logical progression. The trajectory of an air mass may reflect both its source and rainout history, and therefore represent a controlling variable in isotopic behaviour which is not adequately described by temperature and rainfall totals alone. It is suggested that air mass source and rainout history is less important in continental areas where all masses undergo considerable alteration in their passages over land. In the absence of distinctive topographic barriers, this may result in a relative convergence of air mass characteristics, whatever

their directional source. Over the U.K., in contrast, isotopic evolution of an air mass prior to its arrival at any location may vary considerably according to its passage over land or sea, and masses may originate from a wide variety of sources.

In this highly variable environment, an examination of air mass influence at a weekly timescale seemed appropriate, since this is the scale at which synoptic features are observed to develop and disperse in the maritime mid-latitude climate (although it is recognised that upper air features may persist for longer, eg. the average periodicity for a Rossby wave in the northern hemisphere winter is 3-8 weeks; BARRETT, 1974). The scale chosen is intermediate between the monthly scale air mass examinations of HÜBNER et al. (1979) in East Germany, and those on a storm-to-storm basis of SMITH et al. (1979) in California, and also of LAWRENCE et al. (1982) on the NE Seaboard, U.S.A. Respective problems of the over-grouping of synoptic climatic data at the monthly scale and of summation of dynamic meteorological data at the storm-to-storm level were apparent in these studies. The outcome of the $\delta^{18}O$-air mass examinations here may direct the choice of a timescale suitable for further studies of isotopic input variations in the U.K. situation.

Classification of air mass circulation patterns over the U.K.

BELASCO (1952) distinguished twenty-three types of air mass which influenced weather characteristics in the U.K. Many of these are the sub-types of five major categories: (1) maritime polar air (mP); (2) maritime tropical air (mT); (3) continental tropical air (cT); (4) continental polar air (cP); (5) continental arctic air (cA). Typical trajectories of these principal air masses are shown in fig. 4.20; summaries of their characteristics, in terms of the weather associated with them, may be found elsewhere (PERRY, 1976; BARRY & CHORLEY, 1976). Isotopically, the importance of such a classification lies in its relationship with air mass origin and probable rainout evolution, according to the Rayleigh model

principles. These are dependent upon the history of air mass heating or cooling from the surface, moisture content and vertical stability.

An important development in the classification of weather types over the U.K. was that of circulation patterns proposed by LAMB (1972), and which was concerned (p.5)

> "... with the positions of the surface pressure centres and tracks along which they are steered by the upper winds controlling the character of the weather sequence over the British Isles, over several days ..."

Classifications according to this system are available on a daily basis for 1961-1971 (LAMB, 1972) and for dates after 1971, quarterly summaries are published in the journal 'Climate Monitor'. This data was therefore convenient for use in this study. The twenty-seven composite categories used by LAMB were reduced for the purpose of this study into the principal directional categories of N, E, S, W, NW and the non-directional categories of C (cyclonic), A (anticyclonic) and U (unclassifiable). This reduction was similarly performed by STOREY (1982), who reviews the mean distribution of circulation types, and associated temperature and rainfall statistics, on a month by month basis, using the LAMB classification.

Table 4.15 provides a summary of weather types associated with the circulation types, and their possible corresponding air mass classifications. On the basis of the Rayleigh model, we may expect precipitation derived from seaward direction circulations (eg. W, NW) to be isotopically heavier than those which have already undergone rainout over land masses (eg. S, E, A) or rainout associated with active synoptic development (especially C).

Statistical manipulation of air mass data

Since weekly $\delta^{18}O$ values were to be compared directly with circulation types, it was necessary to weight the occurrence of a circulation category by the precipitation produced on that day. In this way, the bias of certain synoptic patterns which produce greater depths of precipitation is allowed for in statistical manipulations.

Two approaches were considered:-

1. A qualitative examination of $\delta^{18}O$ values sorted according to the dominant circulation type, to identify any significant properties of isotope input at the synoptic scale, which may be useful for input prediction purposes and also retrodictive assessment of palaeohydrological inputs.
2. A more detailed examination by modelling of $\delta^{18}O$ using a multiple regression model, to attempt increased explanation of the weekly $\delta^{18}O$ values, either to replace or to supplement the temperature and amount isotopic effects previously considered in a linear regression model (section 4.2.2(c)).

Qualitative assessment of $\delta^{18}O$ values associated with dominant circulation types

Figures 4.21 and 4.22 show the division of weekly precipitation amounts into the 8 circulation type categories. The dominant type for each week is chosen as that contributing the maximum percentage to total weekly precipitation. It is evident that the majority of weeks are hybrid (dominant type precipitation < 100%) but the dominant circulation type rarely accounts for less than 50% of the precipitation total. Westerly and cyclonic circulations are most prominent in precipitation production over the U.K., a factor well noted by STOREY (1982).

By comparison of figs. 4.21, 4.22 with figs. 4.6 and 4.7 of weekly $\delta^{18}O$ variations, it is evident that a wide range of $\delta^{18}O$ values may be associated with each circulation type. For example, extremes of $\delta^{18}O$ have occurred in periods of undefined/unclassifiable (U) circulation, -17.3 $^{o}/_{oo}$ in February 1981 and -2.7 $^{o}/_{oo}$ in August 1981, and both light (September 1981) and heavy (December 1981) $\delta^{18}O$ values are found with southerly circulations.

Histograms of weekly $\delta^{18}O$ sorted by circulation type (fig. 4.23) show very clearly the wide spread of isotopic input in each category. These

distributions wil be considered next, with respect to meteorological conditions associated with each circulation type, which are summarised in table 4.16, and also with respect to probable synoptic conditions.

The mean of westerly circulation $\delta^{18}O$ values (-7.2 $^{o}/_{oo}$) is slightly heavier than the overall mean annual input value (-7.6 $^{o}/_{oo}$; table 4.13). The heavier mean may be due to westerly airstreams tending to produce their initial rainout which is isotopically enriched, over the U.K. Westerly circulation exhibits the smallest $\delta^{18}O$ standard deviation, possibly indicating relative constancy in source and rainout history characteristics. The high standard deviations of other (smaller sample) categories lowers the possibility of identifying significantly different groupings of $\delta^{18}O$ values, but it is interesting to examine the defined distributions in qualitative terms of probable synoptic conditions.

Cyclonic circulations, frequently associated with heavy precipitations, have a light mean (-8.4 $^{o}/_{oo}$), and an almost square distribution. It is possible that rainout prior to precipitation over the U.K. causes the shift in mean relative to other circulations, and that variations in degree of rainout (assuming a uniform initial condition) cause the scatter.

Southerly circulation precipitation appears rather isotopically light (mean -8.1 $^{o}/_{oo}$) with respect to its mean temperature (7.5^{o}C), although the multimodal distribution makes the use of mean values rather misleading. South and south-westerly airstreams in this category might bring isotopically enriched (warm source, air mass mT) water vapour which first precipitates over the U.K., as in westerly circulations. The occurrence of an extemely light winter value (an outlier in fig. 4.23) may, however, be due to previous rainout over Europe. Previous rainout is more likely for northerly and easterly circulations, although in summer months, continental evaporation may provide an isotopically enriched source of water vapour, hence the wide spread of the few samples in the N and E categories. This evaporation effect could explain

the high mean (-5.2 °/oo) of predominantly summer (highest mean temperature) anticyclonic precipitation. Isotopically heavy values in north-westerly circulation, despite a cool vapour source, are probably due to the lack of previous rainout (as for westerly circulation).

The large spread of $\delta^{18}O$ values in the U category (σ=3.8 °/oo) reflect a variety of vapour sources and condensation conditions, including summer thunderstorms and snow squalls, which may be associated with unclassifiable circulation conditions.

Certain logical patterns have emerged in a qualitative discussion of the relationships between $\delta^{18}O$ in precipitation and dominant circulation types. A real benefit would be gained in stable isotope studies in the U.K., if this approach could be included in a formal model, to improve prediction and/or post-diction of $\delta^{18}O$ values in precipitation.

Multiple regression modelling using circulation types

The use of dominant circulation type only in consideration of weekly $\delta^{18}O$ variations cannot take into account the possible mixture of specific circulation types which together produce the weekly $\delta^{18}O$ value. Multiple linear regression was attempted, therefore, using the precipitation amounts in the 8 circulation categories as independent variables. Dependent variables examined were firstly the raw weekly $\delta^{18}O$ values (temperature therefore not being taken into account), and secondly residual $\delta^{18}O$ values after multiple linear regression modelling for temperature (WATEMP) and amount (WPPT) effects, the residual values being previously plotted in fig. 4.19.

Results of the forward stepwise linear regression (Appendix B) are shown in table 4.17.

The forward regression on raw $\delta^{18}O$ values stops at step 7, no further inclusion of independent variables adding significantly (at the 50% level) to the explanation of total variance in $\delta^{18}O$. The level of explanation achieved, 23%, is in fact slightly higher than that for weekly precipitation amount

(WPPT) alone. The order of inclusion of variables appears to reflect their dominance in contributing to an amount effect ie. the sensitivity of $\delta^{18}O$ to rainfall in the different circulation categories. Cyclonic rainfall enters the regression first and class U second, both categories exhibiting high sensitivity of $\delta^{18}O$ to amount. Anticyclonic rainfall enters last, the $\delta^{18}O$ value apparently more independent of rainfall amounts. It is interesting to compare the regression coefficients with that computed for the weekly amount effect (ie. -0.039). Higher coefficients are found for those circulations which regularly bring isotopically light precipitations and/or exhibit a strong amount effect (eg. N, E, U, S). Westerly circulation has a lower coefficient (-0.031), reflecting perhaps its tendency to produce isotopically heavy rainfall. Anticyclonic and cyclonic coefficients closely match that of the amount effect.

Seven steps are also produced in the forward regression of residual $\delta^{18}O$ against rainfall amounts categorised by circulation. This time the anticyclonic variable is omitted. The explanation of variance offered by this additional modelling is rather small (maximum, 15%), indicating that other controls of $\delta^{18}O$ variations remain to be found. The regression coefficients, however, follow a logical pattern. Positive coefficients of W and NW categories bearing isotopically enriched vapour with little previous rainout produce positive residuals (ie. $\delta^{18}O$ values heavier than expected from WATEMP and WPPT alone), whereas the airstreams from depleted vapour sources N and E have the most negative coefficients, as would be expected. Intermediate coefficients (close to 0.00, ie. C, W, S) indicate no strong tendency of that particular category to produce $\delta^{18}O$ values significantly different from those predicted by temperature and amount effects.

Summary of circulation type investigations

It appears that a consideration of circulation types has not quantitatively improved our explanation of, or our ability to predict, weekly

$\delta^{18}O$ input variations in the U.K. although the comprehensibility of the coefficients obtained in the regression models is encouraging. Intuitively, an improvement was anticipated in the U.K. situation, where conventional temperature and amount effects appeared to be obscured by some other mechanism. It may be that the particular classification system employed does not adequately reflect the isotopic history of the air mass (in terms of source and previous rainout), and that an alternative index may be more suitable. The introduction of temperature at vapour source and accumulated rainout would be ideal, and further work in this complex area demands co-operation of isotope hydrologists with meteorological scientists, to derive a more isotopically meaningful classification. Without this, interpretation of isotopic data is limited to periods and locations where input monitoring has taken place; extrapolation of input data at the weekly or monthly timescales, on the basis of meteorological information alone is subject to large and unpredictable errors.

4.2.2(e) Assessment of weekly $\delta^{18}O$ variations in precipitation for natural tracing studies in hydrology

Although the driving mechanisms of $\delta^{18}O$ variations in weekly precipitation have not been satisfactorily explained, we must still assess the observed input variations in terms of their utility as traceable concentrations in hydrological studies. This approach assumes that weekly input variations are appropriate for the particular system being studied.

The concept of a 'spike' is introduced as an input concentration significantly different from background concentrations in the system under investigation. In isotopic terms this may be defined as

$$\text{SPIKE} = (\delta_{\text{INPUT}} - \delta_{\text{BACKGROUND}}) \times (\text{input quantity})$$

For examinations of rainfall as input, units are $^{o}/_{oo}$ mm.

The spike may be positive or negative. A strong spike is required in systems where dilution by mixing and/or storage occurs, in order for tracing to be successful.

If it is assumed that the background isotopic level is that of water well mixed over a year or more, we may choose the value of -7.8 $^{o}/_{oo}$ for $\delta^{18}O$ in the Malham area. This corresponds with the monthly mean value weighted for precipitation amount (mean B) at Malham Tarn Field Centre, and also with the mean (fissure storage) groundwater values at Higher Tren House borehole (section 4.3.1).

It is evident from figs. 4.6 and 4.7 that the extreme $\delta^{18}O$ values are frequently associated with relatively small precipitation amounts and therefore are of little use as tracers. Correlations of SPIKE, however, with temperature (WATEMP) is fair and with precipitation (WPPT) is good, with correlation coefficients of 0.37 and 0.47 respectively, both significant at the 99% level (n=102). The WPPT correlation is inflated, however, by multicollinearity (the variable is contained in both dependent and independent variables).

Interestingly, a significant inverse correlation, (r=-0.46, significant at the 99% level) is found with the number of days in which snow fell in each week, the values for which were included in table 4.11. Approximately 40% of all weeks at Malham had snowfall (NB: a separate snow sample was not always required for the $\delta^{18}O$ measurement). This suggests that snow may form an important input 'tracer' for stable isotope hydrological studies. Snow exhibits an additional important property in that a release by snowmelt may take place of an equivalent precipitation depth produced by several depression systems, thereby enhancing its 'spike' value. Figure 4.24 shows, however, a frequency distribution of all snow samples taken, revealing that isotopically heavy (near background -7.8 $^{o}/_{oo}$) snowfall is possible as well as the more normal isotopically light values (minimum $\delta^{18}O$ recorded, -24.4 $^{o}/_{oo}$, 14.12.1981).

Extreme care must be taken, however, in the sampling of a snowpack prior to melt for studies in stable isotope hydrology. When snowmelt is accompanied by rain, this also must be sampled. Significant isotopic development may take place even without further precipitation. Hoarfrost, for example, formed on a pack at AERE Harwell (13.1.1982) was found to give $\delta^{18}O$ values at the surface 5.5 $^{o}/_{oo}$ lighter than that of the main pack. In sampling snow cores in the Malham area (4.2.1983) a range from -12.7 to -10.9 $^{o}/_{oo}$ was detected in 5 samples taken within an area 1 km^2. It is evident, therefore, that a tracing 'spike' in snowmelt cannot be relied upon, nor used indiscriminately. Its use is obviously precluded from studies in the U.K. which require assessment of hydrological behaviour in the summer months. It has been shown in this section, however, that significant deviations from mean stable isotopic values, with a greater range than those found in monthly samples, are available in weekly precipitation in the U.K. for hydrological studies.

4.2.3 Within-storm sampling of precipitation

4.2.3(a) Introduction

A total of 16 four-day sampling runs were made for the examination of within-storm isotopic variations. Of these, only 7 provided samples of sufficient quantity and continuity, and these are presented in figs. 4.25 - 4.28. Two locations of sampling are reported: the site of AERE Harwell (NGR SU 474866) and King's Norton, S. Birmingham (NGR SP 043797). The sampling was carried out to consider (a) the patterns of within-storm variation under different synoptic conditions, and in comparison with the theoretical model presented schematically in fig. 2.21; and (b) the range of shorter period isotopic variation which may be available for natural tracing studies in the U.K.

Although requiring a larger minimum volume for standard measurement (5 ml, or 0.4 mm precipitation through a 5" diameter funnel), $\delta^{18}O$ determinations

were made in preference to δD, for the sake of comparability with weekly and monthly precipitation and with the majority of ground and surface water isotopic determinations.

A volumetric check on the catch of the automatic sampler used for these studies was made against continuous rainfall records, taken approximately 350 m away, on the site of AERE Harwell for December 1982 and June 1983. 2-hourly sampling volumes were consistently in close agreement, to $\pm$0.1 mm, with volumes read from hyetographs. The agreement of catch between the King's Norton site and a continuously recording raingauge at Winterbourne, Birmingham (NGR SP 058845, $\sim$4 km NNE of King's Norton) was less good, possibly reflecting the localised nature of summer precipitation in an urban area (especially in the thunderstorm of 19.8.1982). The check gauge is useful however to indicate the amount by which the sampling bottle's capacity was exceeded. The maximum capacity of the 30 ml glass sampling bottles corresponds with a catch of 2.4 mm. Where this was exceeded, isotopic measurement of overflow water was made and normally a close agreement of isotopic amounts weighted from individually overflowing bottles was found. $\delta^{18}O$ results presented, therefore, remain those of the full bottles measured, without adjustment for overflowing. It is noted, however, that for short-period, intense rainfalls, a system of equal quantity (eg. tipping bucket) sampling might be more appropriate, to gain better resolution of isotopic evolution of precipitation during such events.

Plots of daily $\delta^{18}O$ values, collected from a daily reporting raingauge (Malham Tarn Field Centre) are shown in fig. 4.29 (a) and (b).

4.2.3(b) Results and discussion

All plots of the 2-hourly sampling of precipitation show variations to occur at this timescale which were masked in the collection of weekly composite samples. The variations observed within a week (between and within storms) are significant, but smaller than those variations observed between weeks, on an annual basis; eg. ranges are seen of only $7\,^{o}/oo$ (fig. 4.25), $9\,^{o}/oo$ (fig. 4.26), $4.3\,^{o}/oo$ (fig. 4.27) and $5.6\,^{o}/oo$ (fig. 4.28).

Western and cyclonic circulation patterns dominate all those storms reported. Frontal rainfall is the most common, and distinct isotopic differences are seen between different frontal types, eg. an occluded front being isotopically lighter than a cold front (figs. 4.25, 4.26). No consistent isotopic difference is found, however, between a warm and a cold front. Rainout has normally already occurred from vapour derived from an occluded front (which tends to be most consistently an 'old' front), and therefore the remaining moisture is isotopically light. A cold or warm front, approaching from a westerly direction may each have undergone little or no previous rainout, and this factor may dominate the isotopic content of precipitation produced, rather than any temperature or source-related effect.

A pattern of isotopic depletion with continuous frontal precipitation, as depicted in the schematic model in section 2.3.2(e), is best seen in occluded (figs. 4.25, 4.26) and cold (figs. 4.26, 4.28) frontal precipitation. This depletion frequently corresponds with an increase in rainfall intensity through these particular rainfall types. Warm front and thunderstorm (summer instability) rainfall $\delta^{18}O$ patterns through time (figs. 4.28, 4.27) appear more erratic. This may be attributable to the stronger vertical motion (updraughts) in precipitation formation in warm, moist and therefore unstable air. It is interesting to note, also, that within these cases, a relative amount effect is apparent within particular storms (especially seen at AERE Harwell, 19.12.1981, fig. 4.28). In the absence of δD data, it remains contendable whether this correspondence of smaller precipitation amounts with heavier $\delta^{18}O$ values actually reflects re-evaporation effects from falling raindrops.

Direct comparison of isotopic patterns in precipitation with synoptic charts - shown in fig 4.30 (a),(b),(c) to correspond with figs. 4.25, 4.27, 4.29(b), respectively - assists in interpretation. The cold front of the

well-developed low passed quickly from the N. Atlantic over central England on 12.8.1982. The occluded front following had a complex formation associated with a secondary low, and bent back SW towards the previous fronts. It had traversed Scotland and northern England before bringing isotopically depleted precipitation in the Midlands. The frontal system of December 1982 (fig. 4.30(b)) is rather more vigorous, and may account for the smaller isotopic distinction between the warm and cold fronts. Interestingly, a clear amount effect is seen in the warm front precipitation, the greatest isotopic enrichment coinciding also with a rise in temperature. It is possible that the following drop in $\delta^{18}O$ and temperature actually indicates precipitation derived from the cold front, the later showers occurring due to cold sector instability with the passage of air from over the relatively warm sea to the cooler ground, in a strong cyclonic westerly circulation.

The coarse timing of daily collections (fig. 4.29) resulted in a combination of precipitation types being collected in individual samples. this loss of fine structure was likely to produce an intermediate range of isotopic variations, although, fig. 4.29 shows that the dominance, for example, of cold frontal snow on one day (1.2.1983) may still produce a dramatic response in $\delta^{18}O$ daily input. The synoptic patterns associated with this sequence (fig. 4.30(c)) show well the influence of shifting circulation types on $\delta^{18}O$ on a daily basis. The north-westerly circulation snow showers were localised, on high ground, and the freshness of this vapour source gave isotopically heavier precipitation than normally expected from this direction. It is possible that the inclusion of cold front precipitation in the sample for 4.2.1983 accounts for its isotopic depletion.

To summarise, a fine structure of isotopic variation has been detected in the short period sampling of precipitation. $\delta^{18}O$ values appear to be related to a combination of isotopic effects and circulation types. Although no strong distinction has been found between cold and warm frontal precipitation,

the limited data indicates that occluded fronts may provide strongly depleted precipitation, and this may be useful in planning hydrological tracing studies. No regular pattern of isotopic progression has been detected, however, as was suggested in a schematic model (fig. 2.21), and an even finer resolution sampling scheme would be required to explain the erratic patterns observed in terms of condensational/post-condensational dynamics.

4.3 Isotope signals in monthly samples of surface and groundwater

The major $\delta^{18}O$ results from monthly samples of surface and groundwater are presented in figs. 4.31 (Malham area) and 4.32 (Lambourn area). In both data sets, observed variations in the stable isotope are significantly reduced relative to those seen in precipitation, at either the weekly or the monthly scale. The total $\delta^{18}O$ range in monthly precipitation noted in section 4.2 has been reduced by 57% to a range of 3.9 $^{o}/_{oo}$ in Malham area surface waters and by 88% to a range of 1.0 $^{o}/_{oo}$ in Lambourn area surface waters. $\delta^{18}O$ variations in Malham area surface waters appear in most locations to be of an erratic nature. Surprisingly a signal more strongly seasonal even than that found in precipitation is evident at the Tarn Outflow, and at the Airehead (North) spring, to which the former feeds. This demands further investigation. The groundwater pumped from Higher Tren House borehole has an almost constant isotopic composition, hardly exceeding measurement error. This pattern of relative invariance is found at nearly all sites in the Lambourn area; the isotopic input signal appears to be almost totally lost at these points in the hydrological system.

More detailed analysis of $\delta^{18}O$ patterns is evidently required, to assess the utility of their application in the U.K. Results of analyses for stable isotopes ($^{18}O/^{16}O$, D/H, $^{13}C/^{12}C$) and for tritium will be presented and discussed below, for each of the sampling areas, together with results of conventional hydrological measurements. The relationships of $\delta^{18}O$ variations

with $\delta^{18}O$ in precipitation, with $\delta^{18}O$ at other sites and with conventional hydrological parameters, will be examined in detail in section 4.3.2.

4.3.1 Results of monthly isotope and conventional hydrological measurements

4.3.1(a) Malham area results

Oxygen-18

In addition to monthly $\delta^{18}O$ variations at the seven main sampling sites (fig. 4.31), results are presented of sites sampled relatively infrequently in fig. 4.33. Numerical results for all sites are given in table 4.18.

The smaller ranges of $\delta^{18}O$ values in all surface and groundwater samples, relative to those in precipitation have already been noted. The range at Waterhouses spring, for example, is from -9.6 to -6.8 °/oo, and is from -9.6 to -7.0 °/oo at Malham Cove. Summary statistics of $\delta^{18}O$ values are included in table 4.19, which gives details of mean, standard deviation, coefficient of variation and the number of observations upon which calculations are based.

The smallest variations in $\delta^{18}O$ observed are at Higher Tren House borehole, which is thought to extract water flowing in fissures. The low standard deviation of 0.11 °/oo, compared with 1.39 °/oo in precipitation at Malham Tarn Field Centre indicates that the input water has undergone considerable mixing before it reaches this point.

The highest standard deviations, are found to occur at Malham Cove, Tarn Outflow and Knowe Fell, where each is of the order of 0.6 °/oo. The spring sites of Airehead (North) and Waterhouses show relatively subdued patterns (σ, 0.5 °/oo) with even further reduction of variability with respect to precipitation occurring in Smelt Mill sinking stream (σ, 0.3 °/oo).

The majority of monthly isotopic plots show rather erratic $\delta^{18}O$ variations, but with lighter values in certain winter/spring months forming the major characteristics, eg. of Knowe Fell sinking stream in January 1982, and of Smelt Mill and Malham Cove in May 1981. Values noticeably heavier than the mean area $\delta^{18}O$ value weighted for total precipitation, of approximately -7.8 °/oo, rarely appear.

In contrast to these observations, however, are the strongly seasonal patterns in $\delta^{18}O$ at the Tarn Outflow and at the Airehead Springs (North and South). Two annual cycles are clearly seen at these sites, with minimum $\delta^{18}O$ values in March/April 1981 and February-April 1982. Maximum values in August/September contrast with other sites by very clearly exceeding average annual $\delta^{18}O$ input values, with levels in the Tarn Outflow waters of -5.9 $^{o}/_{oo}$ (start of September, 1981) and -5.7 $^{o}/_{oo}$ (start of August 1982).

Arithmetic averages of monthly spot measurements from discrete sampling of waters cannot be expected to be directly comparable with input averages calculated from accumulated storage of precipitation, since fluctuations at the ground and surface water sampling sites between sampling visits, in terms of both isotopic concentration and amount of water (stream discharge), cannot be taken into account. $\delta^{18}O$ means, however, (table 4.19) are generally close to weighted precipitation means, if the special cases of Tarn Outflow (mean, -7.0 $^{o}/_{oo}$) and Airehead Spring (mean at North spring, -7.3 $^{o}/_{oo}$) are excluded, and range from -7.5 to -7.8 $^{o}/_{oo}$.

At-a-site variations of $\delta^{18}O$ through time will be considered as a response to precipitation input signals, in relation to other sites and in conjunction with conventional hydrological measurements in section 4.3.2(a), after results have been presented for other isotopic measurements and for the conventional hydrological measurements.

Deuterium

Only a limited number of δD measurements were made, and these are shown in the $\delta^{18}O$-δD plot of fig. 4.34; the plot also includes values for soil moisture but excludes the special case of Tarn Outflow water. Deuterium results are presented in table 4.20. The range of measurements of ground and surface waters is small, δD values clustering around -50 $^{o}/_{oo}$, which corresponds with -7.5 $^{o}/_{oo}$ for $\delta^{18}O$ along the Meteoric Water Line (MWL).

Scatter occurs along both sides of the MWL, and a linear regression of all samples gives the relationship to be:-

$$\delta D = (7.16 \pm 0.41)\delta^{18}O + (4.52 \pm 3.07)$$

for n=44, r=0.94. The importance of these results is to demonstrate the general agreement of the regression with those for precipitation (table 4.4), which indicates a lack of significant modification, eg. by evaporation, of the waters examined. The major outliers marked in fig. 4.34 do not, however, appear to relate to months when precipitation also showed deviations in its $\delta^{18}O$-δD plot (figs. 3.30 and 4.8).

Carbon-13

A limited number of $\delta^{13}C$ measurements, of the total inorganic carbon dissolved in the water, were performed on samples collected in the Malham area. The results are presented in fig. 4.35 and in table 4.21. Two main features of the $\delta^{13}C$ values may be noted:-

(1) different sites appear to exhibit characteristically higher or lower $\delta^{13}C$ values, with respect to other sites; and

(2) seasonal variations in $\delta^{13}C$ are exhibited at the Tarn Outflow, with values isotopically lighter in summer than in winter.

The $\delta^{13}C$ values are all intermediate between those characteristic of soil CO_2 of approximately -26 $^{o}/_{oo}$ (section 3.3.2(c)) and of the Carboniferous limestone in this region of -0.6 ± 0.2 $^{o}/_{oo}$ (THORPE, 1981).

In the Malham area, the waters which best illustrate low $\delta^{13}C$ values, indicative of open system dissolution, are the springs at Waterhouses (mean -14.8 $^{o}/_{oo}$) and at Malham Cove. Closed system dissolution (limited supply CO_2, followed by contact of the infiltrating water with the carbonate rock) would be characterised by higher $\delta^{13}C$ values, as a greater proportion of the dissolved inorganic carbon is derived from the rock. It is suggested, however, that the higher $\delta^{13}C$ values sampled in the Malham area may be due rather to contact and exchange with atmospheric CO_2. This source of carbon

has $\delta^{13}C$ values of -7 to -9 °/oo (MOOK, 198 0). Specific waters sampled are known to have had considerable opportunity for exchange with atmospheric CO_2. This is particularly true of the Tarn Outflow waters and the Airehead Springs to which it feeds. Knowe Fell sinking stream samples may also be affected by this effect, isotopic exchange being enhanced by turbulence of the stream.

Seasonality in $\delta^{13}C$ at the Tarn Outflow may reflect the greater isotopic exchange with atmospheric CO_2 in the summer months, due to the higher temperatures and/or the possibly longer residence times of water in the Tarn. It is probable that the isotopic heaviness of dissolved inorganic carbon in the Tarn in summer, which exceeds levels in atmospheric CO_2, is due at least in part to the precipitation by the aquatic organism Chara of dissolved calcium carbonate. Fractionation results in the isotopically light carbonates being deposited first (USDOWSKI et al.,1979). This phenomenon, however, is also identifiable by conventional hydrological measurements (eg. in the seasonality of alkalinity at the Tarn Outflow), which will be presented later in this section.

Tritium

Tritium concentrations in precipitation input at Malham Tarn Field Centre, and also in selected surface waters, are shown in fig. 4.36, and listed in table 4.22. Early precipitation data (April to October 1980) are taken from THORPE (1981). Sampling periods correspond with those used for the collection of stable isotopes, and therefore precipitation amounts of table 4.1 are applicable, for the latter part of the collection period presented.

The seasonal variation of tritium in precipitation is clearly seen. The range of variation observed is from 12 to 66 TU. High concentrations occur in spring when the troposphere 'turns over'. The exact timing of this event, which brings in higher tritium concentrations from both natural and (remainder of) bomb-test sources, varies between the months of March to June. In 1982, the peak in June appears to be subdued in comparison with other years,

representing only 3 times the minimum value, in comparison with the 4-fold increase found in 1980 from trough to peak.

Tritium levels in surface waters in the Malham area all exceed 1 TU and therefore must post-date the first bomb test and/or be a mixture of old and recent waters (section 3.3.1(b)). The range of values observed in surface waters from 15 to 71 TU actually exceeds that in precipitation. Two explanations are possible of the higher maximum, observed at Airehead Springs in August 1982:

(1) the tritium concentration is a response to greater and shorter period variations in tritium input, not observed at the monthly scale collection of precipitation; or

(2) the baseflow component, derived from older waters in which (bomb-produced) tritium levels remain higher than current precipitation levels, accounts for the increase in TU between Tarn Outflow and Airehead Springs.

There appears to be an absence of studies of short period variations of tritium in precipitation to corroborate suggestion (1), however, the contribution of recent precipitation to springflow at the time of sampling appears unlikely. Only 19.6 mm of precipitation had fallen in the previous month (July), 0.1 mm of which was effective rainfall. Additionally, as will be shown in section 4.3.2(a), the Malham area surface waters were not in general found to be responsive to the (larger amplitude) weekly $\delta^{18}O$ variations in precipitation but reflected subdued values in even monthly precipitation $\delta^{18}O$ values; it seemed unlikely therefore that a short period response could be attributed to observed tritium values.

The second suggestion of older baseflow appears more likely. Flow was very low in August 1982, the northernmost spring at Airehead being dry, and the sample being taken from a small baseflow at Airehead spring South. This confirms observations in $\delta^{18}O$ which also indicated a high baseflow contribution to the lower spring, in this month.

No tritium levels in precipitation recorded since November 1977 at Malham Tarn Field Centre (THORPE, 1981, his fig. 3.22; fig. 4.36, this study) have exhibited ^{3}H concentrations as high as the observed 71 TU at Airehead. The conclusion is drawn that, from $\delta^{18}O$ evidence, baseflow is well mixed over an annual timescale and from tritium evidence, water more recent than 1952, and also water older than 1978 is contributing to baseflow. The baseflow component accounts for the higher tritium levels observed in fig. 4.36 at the Airehead Springs relative to their known feeder of the Tarn Outflow water.

In the above examination of baseflow levels, both tritium and the stable isotopes were acting as conservative tracers. Where the stable isotopes appear to undergo exchange with their environment, and therefore are not conservative - in the passage of water through Malham Tarn - the tritium results provide a valuable conservative indicator. From comparison of monthly sampling at Waterhouses Spring (a 'representative' input to the Tarn) and at the Tarn Outflow stream, a lag in tritium variations is apparent across the Tarn, of approximately one month. Most noticeably, for example, a trough in tritium at Waterhouses in July 1982 is observed at the Tarn Outflow in August 1982 (fig. 4.36). This important information provided by tritium will be further considered in relation to the stable isotope signals observed in the Tarn, with respect to conventional hydrological information, in section 4.3.2(a).

Hydrological measurements and chemical analyses

Summary statistics of hydrological measurements and chemical analyses for each of the seven major sites are given in table 4.19.

The largest percentage variations with respect to mean values (ie. coefficients of variation) are found in discharge, and the smallest in pH. The (modulus of the) coefficient of variation in $\delta^{18}O$ at each site tends to be lower than that found in alkalinity, Ca^{2+}, conductivity, discharge or

temperature. The coefficient of variation in alkalinity may be taken in this study to be representative of that of water hardness as $CaCO_3$, due to the high co-variance between the variables and due to the completeness and reliability of the alkalinity data set. In the schema used by SHUSTER & WHITE (1971) discussed in section 1.4.1, we find that all the spring sites sampled could classify as conduit feeder type springs, since coefficients of variation in the Malham surface waters are all above 10%. The highest, of 85% is found at Waterhouses. Water intercepted at Higher Tren House would classify as being derived from predominantly diffuse flow using this system, due to its low coefficient of variation.

In fig. 4.37 ((a) to (g)), in which conventional data are plotted for each site, a seasonal component may be detected in particular variables. These are notably temperature and alkalinity. The strength of seasonality in temperature is dependent upon the shallowness of flow, or presence of overland (especially allogenic) components of flow. A deep and/or authogenic flow tend to produce a more constant water temperature, the slowness of flow contributing to the averaging out of seasonal surface temperature fluctuations by the mixing of water and also by heat exchange with the aquifer rock matrix, which at depth tends towards a constant (approximately mean annual) temperature, at the timescale of this investigation. Only small temperature variations are seen, for example, at Waterhouses Spring.

Where carbonate rock dissolution is predominantly controlled by the production of CO_2 resulting in carbonic acids and also in the production of humic acids in the soil horizon, seasonality in alkalinity so produced reflects the seasonal cycles of plant and organism activity. Peaks in alkalinity in the Malham area are observed in August/September, and minimum levels in January/February/March. According to this mechanism, calcium concentrations would be expected to follow a similar pattern. This is the spring 'burst' in water hardness which PITTY (1968) recognises from monthly

sampling of the Gordale Beck (Malham area). Unfortunately too few Ca^{2+} determinations are available to provide exactly comparable data although this effect is observed in the more reliable alkalinity data.

Conductivity at most sites follows the same general pattern of variation as found in alkalinity, as expected in predominantly carbonate waters, but with small deviations, due, perhaps to (1) the contribution of other ions (eg. Cl^-, NO^{2-}_3, Na^+, K^+ and H^+ and organic radicals) to the conductivity of the solution, and/or (2) small fluctuations in machine calibration within a sampling run, which remain uncorrected.

The sensitivity of pH to the total suite of ions in solution may make interpretation of this parameter misleading unless a full chemical analysis is available. In general, however, a higher pH (more alkaline solution) is expected and observed with the increased dissolution of carbonate materials, eg. in the summer months.

Superimposed on a seasonal pattern at each site are individual hydrological events. Each major site will be examined for these, which are evidenced by fluctuations in temperature, discharge and/or water chemistry, in section 4.3.2(a). Monthly spot sampling may be of any part of a hysteresis curve (eg. rising or falling limb), therefore consistent direct relationships between the parameters cannot reasonably be expected.

4.3.1(b) Lambourn area results

Oxygen-18

Figure 4.32 and table 4.23 present the $\delta^{18}O$ results of monthly sampling of the Rivers Lambourn and Winterbourne, and groundwater extracted from boreholes, in the Lambourn area. Characteristic of all the $\delta^{18}O$ plots is the great attenuation of the input signal previously observed in precipitation (figs. 4.4, 4.5), and in many cases the observed variations hardly exceed experimental error. All $\delta^{18}O$ values fall within the range -8.3 to -6.7 $^{o}/oo$

Table 4.24 provides summary statistics for the 9 major sites. Standard

deviations fall in the range 0.1-0.2 °/oo, in contrast with that in monthly precipitation of 2.3 °/oo for the combined datasets of Lechlade (October 1980 - December 1981) and Warren Down Farm (January - December 1982) (n=24). The attenuation of $\delta^{18}O$ variations in the Lambourn area is greater than that observed in surface waters of the Malham area, but comparable with attenuation observed in water extracted from the Higher Tren House borehole.

$\delta^{18}O$ observations in the Lambourn area are consistent with the generalisation that flow through chalk is predominantly diffuse, and therefore allows ample time for complete mixing of waters, at least over an annual timescale.

Mean values of $\delta^{18}O$ at most locations in the Lambourn area fall in the range -7.5 to -7.4 °/oo, which corresponds with values intermediate between the arithmetic and monthly total precipitation-weighted means of input (of -7.3 and -7.8 °/oo respectively for Warren Down Farm data, table 4.5). Exceptions are at Manor Farm borehole, where heavier waters are found (mean -7.1 °/oo) and at Oakash borehole, where the groundwater sampled is significantly lighter (mean -8.2 °/oo).

The heavier $\delta^{18}O$ values at Manor Farm may be due to evaporation, since the water level is relatively close to the surface (only 0.4 to 1.6 m below the borehole flange plate), and strong seasonal variations in borehole water surface temperature were observed through the study period. $\delta^{18}O$ does not follow a distinctly seasonal pattern, however, which would be the case were evaporation operating. An alternative explanation might be in the alteration of mean $\delta^{18}O$ associated with the area of water meadow peat (alluvium) soils, which will by considered in section 4.4.1.

Two explanations of isotopically light values at Oakash may be suggested:-

(1) Net evapotranspiration is more efficient in the upper catchment, resulting in a total loss of (isotopically heavier) summer

precipitation and a tendency in recharge $\delta^{18}O$ towards the lighter effective precipitation-weighted mean. Groundwater sampled in valley locations, including the upper dry valleys at North Farm and Ashdown Park, receive isotopically enriched summer precipitation in their recharge waters, and therefore are isotopically heavier.

(2) Water being sampled at Oakash is different because it derives from a different past climate to water sampled elsewhere in the Lambourn catchment.

Relevant to suggestion (1), BATH et al. (1984) observed a shift of 5 $^{o}/_{oo}$ from the mean weighted δD in precipitation in water recharging through Chalk in Cambridgeshire under arable agriculture. The exact source of the shift was not clear, although in the Lambourn area $\delta^{18}O$-δD plots (see below) do not indicate partial evaporation to play a very significant role in any of the groundwaters examined. For a better indication of spatial variations in the water balance being reflected in the isotopic composition of groundwater, a more full sampling net of boreholes, perhaps in a one-off survey, would be required.

With respect to suggestion (2), water at Oakash near the crest of the water table, may represent the most recent recharge; groundwater flowing through valley-sited boreholes and discharging into the Rivers Lambourn and Winterbourne may represent older water. In this case the climate associated with the older water was relatively warmer. If, however, age of groundwater is controlled by depth of unsaturated zone through which water must slowly percolate, before entering the zone of more rapid transmisison in the saturated zone, then water at Oakash would represent the oldest water in the catchment, the depth through chalk to the water table being greatest at this location of all the sites sampled. In this case the older climate is relatively colder (water derived from isotopically lighter precipitation). The isotopic difference of 0.7 $^{o}/_{oo}$ in $\delta^{18}O$ between waters in either case

indicates a difference in mean annual temperature between the climates of approximately 1°C, if the DANSGAARD (1964) relationship (equation 2.16) is applied.

Depth sampling of the boreholes was undertaken to examine the possibility of $\delta^{18}O$ stratification associated with depth of saturated aquifer. Results are shown in fig . 4.39 for sampling in March/April, May and August, 1981. The overall observation is that $\delta^{18}O$ variations with depth in each of the boreholes are generally within experimental error. Only at Oakash borehole (fig. 4.39(e)) are variations greater than ± 0.2 °/oo. A lighter isotopic water at depth (at 90 m below well-head) is found in the samping of April 1981, possibly indicating stratification of water stored in the saturated zone. Conventional hydrological information (water chemistry and temperature data) are, however, unable to provide any additional information. At the levels of precision achieved in this study, the water appears in individual boreholes chemically homogeneous and at most locations is at constant temperature (within measurement error) below 20 m from the surface.

The statistical relationship of the monthly $\delta^{18}O$ measurements at each site with respect to the input signal in precipitation, with respect to each other, and in relation to conventional hydrological data will be discussed in section 4.3.2(b).

Deuterium

Samples of ground and surface water which were analysed for both $\delta^{18}O$ and δD are plotted in fig. 4.40, and δD results given in table 4.25. All δD values fall in the range -59 to -44 °/oo and a clustering of values occurs around -50 °/oo (δD) and -7.5 °/oo ($\delta^{18}O$). Linear regression of δD against $\delta^{18}O$ gives:-

$$\delta D = (7.64 \pm 0.96)\delta^{18}O + (6.56 \pm 7.26)$$

for which the correlation coefficient (r) value is 0.78 (for n=42). There are no significant differences between the regression slope and intercept values

and those of the Meteoric Water Line (MWL). The majority of points plotted in fig. 4.40 fall within experimental error of the MWL. The ground and surface water sample values may therefore be assumed to exhibit no significant difference from the $\delta^{18}O$-δD relationship current precipitation in this area.

No consistent patterns of slope decline, attributable to evaporative enrichment, are evident. The position of the two Manor Farm borehole samples (March 1981, August 1981) either side of the MWL does not indicate evaporation from a constant isotopic value. The difference in δD may, however, be related to recent rainfall inputs, possibly altered in passage through the water meadow peats (section 4.4.1), as previously considered.

The differences in Oakash borehole waters at depth from borehole 'top' waters (indicated by no depth being marked) in April and June 1981 may reflect different water ages, as previously discussed. This being the case, more recent (upper) waters have a slightly lower d-excess parameter, which would indicate higher kinetic evaporation rates at water vapour source to be associated with the older water. If this is tenable, groundwater feeding the Lambourn system, and also the scarp foot Woolstone Springs to the North, falls in the older category of water. Such suggestions, however, remain speculative, in the absence of further δD (and $\delta^{18}O$) groundwater surveys.

Carbon-13

A limited number of $\delta^{13}C$ measurements were performed, principally on river Lambourn waters, and these are presented in table 4.26. The most notable features of these measurements are:-

(1) The generally high $\delta^{13}C$ values (in comparison with the Malham area springs), in the range -12.3 to -14.0 $^{o}/_{oo}$.

(2) The small degree of variation observed at each site, eg. range 0.5 $^{o}/_{oo}$ at Shaw, falling almost totally within experimental error of $\pm$ 0.3 $^{o}/_{oo}$(at 1σ).

(3) The apparent downstream increase in $\delta^{13}C$; the mean rises by 0.8 $^{o}/_{oo}$ from source to the river Lambourn at Shaw.

The Chalk in this region has a $\delta^{13}C$ value of approximately 2.4 $\pm$ 0.05 $^{o}/_{oo}$ (D.B. SMITH et al., 1976). From a simple mass balance calculation, it would appear that approximately 56% of the carbon in the Lambourn chalk waters, with mean $\delta^{13}C$ of approximately -13 $^{o}/_{oo}$ is derived from the rock; the remaining 44% of carbon is from soil CO_2, assumed to have a $\delta^{13}C$ value of -26 $^{o}/_{oo}$. The system of solution in the chalk may be classified, therefore, as being less 'open' relative to systems feeding springs in the Malham area, which exhibit lower $\delta^{13}C$ values.

Interpretation is complicated further, however, by subsurface processes of secondary carbonate dissolution in the near-surface zone (GEYH, 1970) and of incongruent deposition/dissolution processes at depth. The latter effect is being investigated for a sandstone aquifer at AERE Harwell (see preliminary results in EVANS et al., 1984) and both processes are important in their implications for effective carbon-14 'dating' of groundwaters.

Where flow is predominantly diffuse and solution kinetics steady through time, a fairly constant $\delta^{13}C$ value may be expected, as observed in the Lambourn area. The downstream $\delta^{13}C$ increase may possibly be attributed to removal of the isotopically lighter carbonates either by outgasing and/or by the precipitation of calcium carbonates out of solutions which are at or near saturation with respect to calcite. The in-mixing of atmospheric CO_2 (mean $\delta^{13}C$ -6.6 $^{o}/_{oo}$) would equally raise dissolved carbonate $\delta^{13}C$ values.

Tritium

A small number of river water tritium mesurements made over the monitoring period are shown in fig. 4.41 together with measurements performed by the Isotope Measurements Laboratory, AERE Harwell, since the beginning of 1968. Records of tritium in precipitation are given for Milford Haven (CAMBRAY et al. 1968-1982). Early measurements at Welford reveal low ^{3}H levels in the river water when values in precipitation input were relatively

high, eg. stream values in 1971 of 10-20 TU, when precipitation values exceeded 100 TU for 6 months of the year, rising to a maximum of 237 TU in March/April. From evidence of low tritium values in springwater sampled in 1967, PATERSON (1971) drew the conclusion that the bulk of water emerging in springs from the scarp foot of the Berkshire Downs was derived from water which had entered the chalk at least 15 years prior to sampling.

Tritium levels in Lambourn area river waters over the period 1981-1982, in the range 13-43 TU, are seen to be generally higher than earlier levels, whereas precipitation levels have gradually fallen since the 1970s. It is interesting to note individual cases of tritium concentration in river water exceeding those in the previous month of rainfall. It appears that chalk waters from the saturated zone are only just responding, and in a subdued manner, to higher input levels of ^{3}H. Difficulties in exact 'dating' of the groundwater arise, due to the decay of tritium since the originally high input levels, almost to the levels in current input waters, and therefore the two sources are almost indistinguishable, as argued in section 3.3.1(b).

The important difference in input characteristics between ^{3}H and the stable isotopes ($^{18}O/^{16}O$ and D/H) is that tritium exhibits an overall trend of decreasing mean annual concentrations with variations both between and within the years (fig. 4.41) whereas the stable isotopes exhibit variations within the year but approximately constant mean input concentrations from one year to the next. The fact that variations in tritium concentrations do occur in river water indicates that complete homogenisation of the input waters over a scale of several years is not occurring, although the constancy of stable isotope ($\delta^{18}O, \delta D$) measurements demonstrate the water to be apparently homogenised over a period of (at minimum) one year.

Hydrological measurements and chemical analyses

Figure 4.42 ((a) to (i)) shows monthly variations of alkalinity (HCO_3^-, ppm), Ca^{2+} concentration, conductivity, discharge/standing water level (in

boreholes), pH and temperature, for surface and groundwaters in the Lambourn area. Summary statistics of the parameters at each of the nine major sites are included in table 4.24.

Discharge values for Welford, Bagnor and Shaw were taken from Thames Water Authority (TWA) records; all other measurements were made by the author. From comparisons of TWA conductivity analyses and field conductivities presented here, it is evident that the calibration of the meter used was particularly unreliable from February to August 1981 (comparisons available for Bagnor only), during which period conductivities were probably variably higher than indicated. The effect of machine (Simac) drift away from the calibration made at the start of a sampling run is more noticeable in the Lambourn area, due to the higher multiplication factors (higher total conductivities) involved in comparison with the Malham area. These relatively unreliable data are considered to account for the uncharacteristically high standard deviations in conductivity for a region of chalk.

In consideration of the low coefficients of variation in alkalinity (table 4.24), it would appear that all waters - with the exceptions perhaps of Manor Farm and North Farm (Upper Greensand) boreholes - may be classified as diffuse flow derived, according to the schema of SHUSTER & WHITE (1971), as previously discussed in section 1.4.1.

4.3.2 The relationship of $\delta^{18}O$ in surface and groundwaters with other monthly monitored parameters

The relationships of $\delta^{18}O$ values measured in surface and groundwaters with $\delta^{18}O$ values in precipitation will be examined, in an attempt to describe the signal attenuation and therefore the possible viability of the stable isotopes as natural tracers of precipitation. Relationships of $\delta^{18}O$ between sites will be examined, to determine similarities of response especially where sites are known to be connected. Comparison of $\delta^{18}O$ with conventional hydrological data will determine the extra information to be derived using the

stable isotope method, and, conversely will aid in the interpretation of $\delta^{18}O$ results. The Malham and Lambourn areas will be considered in turn.

4.3.2(a) Malham area

Relationship between $\delta^{18}O$ in precipitation and in surface and groundwaters

Results of correlation analysis between $\delta^{18}O$ at sampling sites with $\delta^{18}O$ in precipitation collected over the month previous to sampling are presented in table 4.27. Considerable variation is found, according to which of the three rainfall stations is selected for correlation at a particular site. It is suggested that this reflects the importance of a particular raingauge or collection site in its positive discrimination towards the rainfall types (section 3.5.2) to which the ground or surface water is responding (eg. the bias towards snow collection at Malham Village in December 1981 matching a response to snowmelt at Knowe Fell, in January 1982).

Certain specific relationships, of ground and surface waters with precipitation are, however, discernable, and are considered below in the order of sites in the 'hydrological cascade':-

(1) Moderately high correlation is found between $\delta^{18}O$ in precipitation and in waters sampled from the shallow spring and throughflow system contributing to Knowe Fell sinking stream (mean correlation coefficient, r, of 0.46; maximum r of 0.67 with Malham Village precipitation).

(2) Springs at Waterhouses, West Great Close and Great Close Scar, each emerging at a similar altitude and the former two contributing to Malham Tarn, each show low correlations with monthly rainfall $\delta^{18}O$, no correlation coefficients being significant at the 95% level.

(3) At an altitude similar to waters in (2), however, Smelt Mill sinking stream exhibits a relatively strong linear relationship with monthly precipitation (r value average 0.47); no significant relationship with precipitation is found at Malham Cove springs, to which Smelt

Mill feeds, indicating loss of the precipitation input signal or else considerable modification in water transmission.

(4) The highly significant correlation between Tarn Outflow waters and $\delta^{18}O$ in monthly precipitation (r values of mean 0.59) is worthy of further consideration since input to the Tarn does not correlate with precipitation in the month prior to sampling (observation (2), above). Additionally, it has been shown that a minimum lag of one month occurs for waters passing through the Tarn, from limited sampling of input and output waters for tritium. It is suggested that the smooth $\delta^{18}O$ signal (fig. 4.31(d)) is generated in the Tarn, and governed by the same or similar meteorological parameters which govern $\delta^{18}O$ in precipitation input. Correlation between $\delta^{18}O$ in the Airehead springs, to which the Tarn water has been traced, and $\delta^{18}O$ in precipitation is poor, indicating further signal modification in this stage of the cascade.

(5) The negative correlation coefficient observed at Higher Tren House appears to be a chance result which is not reliable for the drawing of physical conclusions since there are few samples and the majority of variations observed are within experimental error. The correlation coefficients are not significant at the 95% level.

From visual examination of figs. 4.31 and 4.33, illustrating the above cases, but excepting case (4), it is evident that the output isotopic signal is as irregular, if not more irregular, in its pattern through time, as that found in precipitation input. Autocorrelation analysis of data from Higher Tren House and from Waterhouses, shown in the correlograms of fig. 4.43 (a) and (b), illustrate the lack of smoothness in the series in their low autocorrelation at lag 1 month. The Waterhouses correlogram shows no distinct seasonality to be present. The Higher Tren House correlogram is less noisey, with r_L peaks at 6 and 13 month lags, but interpretation is again restricted

by the relatively small variations being examined at this site. In contrast, the correlogram for Tarn Outflow (fig 4.43(c)) describes the strong seasonality of signal, even more emphasised than that found in precipitation (fig. 4.10). High autocorrelation coefficients at low lags at Tarn Outlfow reflect the smoothness of the signal; a maximum r_L value is found of 0.87 at lag 11 months. Enhancement of the precipitation signal, rather than attenuation of the signal, as elsewhere, appears to be revealed at the Tarn Outflow, and will be further analysed later in this section.

In the Malham area, although the isotopic variation at most sampling sites is subdued relative to precipitation, a rapid response to hydrological events is commonly observed in the surface waters. It appears possible, therefore, that the isotopic response is occurring at a timescale of less than one month, a suggestion which requires further analysis of the data available.

$\delta^{18}O$ values in precipitation for the week prior to sampling were correlated against ground and surface waters at the seven major sites, (table 4.27). Decay functions were additionally employed to take into account a response to precipitation in previous weeks, with progressively less weighting for input in the more distant weeks, in the style of the simple models used in antecedent precipitation indices. The weighting of input amount embraces the arguments presented in section 4.2.2(e), when weekly $\delta^{18}O$ input values were considered as tracer 'spikes'. The following simple decay (DEC) functions were chosen on an exploratory basis to calculate a weighted isotope input value:-

$$DEC(1) = \frac{(0.67 \times \delta^{18}O_w + 0.33 \times \delta^{18}O_{w-1})}{(0.67 \times PPT_w + 0.33 \times PPT_{w-1})}$$

$$DEC(2) = \frac{(0.5 \times \delta^{18}O_{w} + 0.33 \times \delta^{18}O_{w-1} + 0.17 \times \delta^{18}O_{w-2})}{(0.5 \times PPT_{w} + 0.33 \times PPT_{w-1} + PPT_{w-2})}$$

$$DEC(3) = \frac{(0.4 \times \delta^{18}O_{w} \; 0.3 \times \delta^{18}O_{w-1} + 0.2 \times \delta^{18}O_{w-2} + 0.1 \times \delta^{18}O_{w-3})}{(0.4 \times PPT_{w} + 0.3 \times PPT_{w-1} + 0.2 \times PPT_{w-2} + 0.1 \times PPT_{w-3})}$$

where subscript w refers to the week of sampling and w-1 to the previous week of sampling, etc., and PPT refers to either total precipitation (indicated by subscript T, eg. $DEC(1_T)$, in table 4.27), or effective precipitation (indicated by subscript E). In each decay function, the weights applied to weekly values add up to unity. The functions employed could be classified as stepped mixed reservoir models (cf. a smooth mixed reservoir model discussed in IAEA, 1983, p. 385).

The greatest improvement in correlation using these decay function models occurs at Knowe Fell sinking stream, for which a maximum correlation coefficient of 0.83 is found using $DEC(2_E)$, indicating an isotopic response to the effective precipitation of up to two weeks previous to sampling. The decay functions are arbitrarily constructed, and further experimentation may improve correlations, and so provide more exact information concerning actual mixing and transit times of water between input (in precipitation) and output. At Waterhouses spring, a small improvement in correlation is made using the chosen decay functions, with maximum r (0.39) using $DEC(3_E)$. The lack of improvement elsewhere, however, using weekly $\delta^{18}O$ input values or a combination thereof instead of monthly values, indicates that the weekly (and extended weekly) timescale is inappropriate for the observed isotopic responses, even in this area where hydrological responses are relatively rapid. Mixing and storage of waters in such areas have perhaps been

underestimated due to the concentration of effort in conventional karst hydrology upon discrete input (sink)/output(spring) systems and upon rainfall response analysis without due consideration of the residence times of actual parcels of precipitation. The stable isotopes may therefore provide an important additional dimension in karst hydrology, as noted by BROWN et al. (1984b); traditional concepts of the karst aquifer may require modification as a result.

Relationships between sampling sites of monthly $\delta^{18}O$ values

Observed correlations between monthly $\delta^{18}O$ values at the surface and groundwater sampling sites (table 4.28) are in general agreement with those expected on the basis of increased mixing and signal attenuation down through the 'cascading' hydrological system. Thus high correlations are found (all r values significant at the 99% level) between Knowe Fell sinking stream and Waterhouses (r=0.60), between Tarn Outflow and both of the Airehead springs (r values, 0.88, 0.70) and between Smelt Mill sinking stream and Malham Cove (r=0.65). High correlations are also found between waters at similar stages in the cascade, indicating their similarity of response to rainfall, eg. high correlations within the cluster of Tarn input springs (West Great Close, Great Close Scar and Waterhouses springs). It is important to note that correlation of stable isotope series between sites cannot in itself provide evidence of a direct relationship (eg. of waters from Knowe Fell to Smelt Mill or to Waterhouses), in contrast with the positive evidence of linkages provided by artificial water tracing techniques.

High correlations of $\delta^{18}O$ in the Tarn Outflow with other waters probably reflects the seasonal dominance of the former's signal, the pattern of which appears to a lesser extent in other waters. Interestingly, the correlation between the Tarn inflow springs and the Outflow water is relatively low (mean r, 0.38). Significantly, no improvement of the correlation occurs if repeated using the $\delta^{18}O$ series for the Outflow, lagged one month behind Waterhouses

$\delta^{18}O$ values (r=0.16) (ie. allowing for travel time through the Tarn, as indicated by tritium). This indicates that processes other than the transit and mixing opportunities may be important in the enhancement of the seasonal $\delta^{18}O$ signal, with passage through the Tarn.

Correlations of $\delta^{18}O$ with waters extracted from Higher Tren House borehole are at no site significant at the 95% level, confirming the severity of signal modification in the water sampled at this location.

Relationships of $\delta^{18}O$ in ground and surface waters with conventional hydrological measurement

Table 4.29 summarises the correlations between $\delta^{18}O$ and values of conventional hydrological measurements measured at each of the major sites in the Malham area. No particular one of the selected six variables is found to correlate consistently and significantly with $\delta^{18}O$. The oxygen isotopes are therefore not simply duplicating the information of conventional hydrological measurements.

Only at the (isotopically and chemically) anomalous sites of Tarn Outflow and Airehead spring (North) is temperature found to correlate significantly (at the 99% level) with $\delta^{18}O$. Temperature as a driving force of $\delta^{18}O$ variations at the Tarn Outflow will be discussed later in this section. The strong seasonality of alkalinity in the Tarn corresponding with that of $\delta^{18}O$ also results in a high correlation coefficient. The only other relationship significant at the 99% level is that between $\delta^{18}O$ and discharge at Knowe Fell, and is inverse; this reflects the stream's responsivity of high flow to winter precipitation which is frequently isotopically light and is evidently transmitted rapidly to the stream. Elsewhere, co-variance is found (to a varying degree) between Ca^{2+}, conductivity and $\delta^{18}O$. Thus dilution effects appear to be accompanied by isotopically lighter surface waters. An exception, however, is at Higher Tren House, where no significant correlations are found with $\delta^{18}O$.

Five particular features may be noted from examination of both conventional and $\delta^{18}O$ plots at each site in the Malham area:-

(1) the return at most sites to a characteristic water chemistry and $\delta^{18}O$ value, in periods of low flow;

(2) the common occurrence of high flows associated with a significant isotopic response;

(3) the less common occurrence of high flows associated with no significant isotopic response;

(4) the apparent persistence into summer of an isotopically lighter baseflow contribution, at certain sites;

(5) the chemical and isotopic distinctiveness of the Tarn Outflow water.

Each of these features and their hydrological implications will be examined in turn.

(1) At most sites, in periods of low flow, a characteristic water chemistry and $\delta^{18}O$ value may be identified. These will be termed baseflow values. Relatively high Ca^{2+} concentrations, conductivity, alkalinity and pH levels are frequently found in these conditions; during the sampling period in the Malham area these occurred notably in March, July and September 1981 and in April to September 1982. It may be assumed that the baseflow is derived from fissure storage, which drains slowly and continuously and is replenished through the year. The characteristic $\delta^{18}O$ levels may therefore represent complete smoothing of the isotopic input signal over one year or more. Interestingly different characteristic levels are found at the various sites sampled in the Malham area (figs. 4.31 4.32, 4.37 and 4.38).

A mean baseflow $\delta^{18}O$ value of approximately -7.5 $^{o}/_{oo}$ is seen at Knowe Fell sinking stream in shallow seepage waters draining through the Yoredale facies; -7.8 o/oo is the apparent baseflow value at Waterhouses spring and is the most commonly measured value at Higher Tren House borehole; an even lighter baseflow value of -8.2 $^{o}/_{oo}$ is observed at West Great Close during

summer 1982. Anomalously at Smelt Mill, a variety of low flow $\delta^{18}O$ values are observed, from -7.8 (July 1981) to -6.9 $^{o}/_{oo}$ (August 1982).

The observed baseflow value of -8.2 $^{o}/_{oo}$ appears to match the average of the annual effective precipitation weighted means computed for this area (table 4.5), and -7.8 $^{o}/_{oo}$ matches exactly the average of means weighted for total precipitation. These baseflow $\delta^{18}O$ values may thus be interpreted as resulting from different recharge conditions, in which the degree of re-evaporation of summer precipitation plays the most important role. This explanation seems unlikely, however, because (1) the opportunity for evaporation from the large areas of bare limestone in the West Great Close catchment appears less than that in the soil-covered area forming (most probably) the Waterhouses catchment; and (2) the isotopically heavier baseflow value at Knowe Fell sinking stream has not been explained by this mechanism.

The baseflow value of -7.5 $^{o}/_{oo}$ at Knowe Fell actually matches the arithmetic mean of monthly precipitation input (table 4.5). This calculated mean has no real hydrological significance, but the match does suggest an alternative hypothesis, dependent upon the surface conditions which receive winter precipitation.

In the upper catchment (eg. on Knowe Fell), soil cover is almost continuous and slopes steep. Winter precipitation may exceed infiltration capacities and thus by-pass the shallow fissured Yoredale limestone aquifer. An isotopic bias may result towards heavier fissure storage. In contrast, where bare areas of limestone outcrop (eg. above West Great Close), recharge to the fissured Great Scar Limestone is direct. No loss of winter recharge occurs, and the resulting baseflow is relatively light. Areas exhibiting a mixture of soil cover and bare karst, as above Waterhouses, might retain fissure storage waters intermediate between the extremes, as observed. Such a mechanism might operate in conjuction with evaporative processes. To test

this proposed hypothesis, more detailed investigations of small area recharge processes are required.

The constant baseflow value identifed at certain sites has practical use in natural tracing studies; it may be used, for example, in hydrograph separations, where isotopic input values are also known, and where chemical parameters, dependent upon solution kinetics, may fail. This technique was tested in storm studies at Waterhouses spring (section 4.5). Where a single baseflow value is not identified, however, eg. at Smelt Mill, the technique may be inappropriate. The hydrological implications of an isotopically variable baseflow will be discussed later in this section.

(2) The association of high flows with a significant isotopic response indicates that the water being transmitted to the sampling point has undergone relatively little mixing since input. Most probably, such water has also undergone little storage, and may be termed 'recent' water (ie. derived from recent precipitation).

This feature is best exemplified at Knowe Fell sinking stream (figs. 4.31(a) and 4.37(a)) for example in May 1981, January 1982 and, to a lesser extent, in October 1982. Respective streamwater $\delta^{18}O$ values are -8.4, -9.4 and -7.1 $^{o}/_{oo}$. The strong statistical relationship of $\delta^{18}O$ at this site with that in precipitation has already demonstrated the stream's responsiveness to recent input. Additionally a chemical dilution effect is seen at this site, eg. of Ca^{2+} in January 1982; this confirms the rapid transmission characteristics. The subdued and erratic $\delta^{18}O$ patterns at Smelt Mill are similar to those at Knowe Fell, also showing clear chemical dilution in high flows (eg. in January and May 1981). In high flow conditions at Waterhouses, an isotopic response similar to that of Knowe Fell is frequently seen. The signal is subdued, however, at Waterhouses, the $\delta^{18}O$ values being drawn towards the baseflow -7.8 $^{o}/_{oo}$. The most dramatic response of -9.1 $^{o}/_{oo}$ at

this site is due to late April snowmelt (sampled at the start of May 1981). It is difficult to determine the chemical dilution effect in this instance, since the minima in alkalinity and conductivity appear to form part of the seasonal pattern. In such a case it would be most useful to have information concerning monthly baseflow (ie. low flow) chemical and isotopic compositions, in order to interpret the meaning of deviations from spot sampling at a variety of stages in hydrological events.

(3) The association of high flows with no significant isotopic response, even though recent precipitation is isotopically distinct from baseflow, is a phenomenon observed most frequently at Waterhouses. In October 1981, for example, flooding occurred at Waterhouses. Streamflow $\delta^{18}O$ at -7.8 $^{o}/_{oo}$ indicated that mixed storage water was probably being expelled at the time of sampling. The corresponding value for precipitation in the week prior to sampling was -8.9 $^{o}/_{oo}$. Importantly, the expulsion of fissure storage is also indicated in the conventional chemical data by relatively high concentrations. In the schema presented in section 1.4.1, the lack of isotopic variance associated with a lack of chemical variance (from periodic sampling), as generally found at Waterhouses and also at West Great Close, clearly indicates the diffuse type of flow. Conventional data, however, could not have shown that the water displaced in flood at Waterhouses had been stored over a period of one year or more.

(4) The apparent persistence of winter-recharge into summer baseflow, identified from isotopic data, is most apparent between the (proven) linked system of Smelt Mill sink to Malham Cove spring.

From conventional data, the subdued temperature regime, higher discharge figures, and lower range of chemical variations at Malham Cove, in comparison with Smelt Mill sinking stream, illustrates the importance of additional flow

components to Malham Cove spring. Modification from input to output in this section of the 'cascade' is greater than is observed between the similarly paired Tarn Outflow and Airehead Springs. Chemical parameters at Malham Cove Spring follow a generally seasonal pattern, with a summer maximum in alkalinity; dilution effects do not always appear to operate.

The most interesting evidence of a baseflow contribution is seen in a comparison of $\delta^{18}O$ at Smelt Mill and Malham Cove (fig. 4.31(e)). A certain co-variance of the $\delta^{18}O$ series is evident ($r=0.65$, $n=25$), and coincidence of $\delta^{18}O$ values is greatest in periods of high flow (eg. in October 1981). Strong deviations between the series occur, however, and appear to persist, especially after periods of substantial and isotopically light input, viz. in the months of May 1981, January 1982 and December 1982. In the first two cases, a negative discrepancy, which is especially strong in subsequent periods of low flow, eg. in July 1981, and in April 1982 is seen to persist for 3-4 months. This observation indicates that the karstified limestone aquifer north of the Malham Cove exhibits incomplete mixing over the annual scale, and therefore produces a seasonally variable isotopic baseflow, which is dominated by light $\delta^{18}O$ values in winter recharge.

The exact location in the aquifer where this incompletely mixed water is stored, whether in the subcutaneous or in the phreatic zone, cannot be determined from the results examined. It may be suggested, however, that incomplete mixing and transmission of winter precipitation down major fissures occurs in a subcutaneous zone, and further, more well-mixed storage occurs at depth, of the type which was sampled at Higher Tren House and which contributes to summer baseflows (eg. in August 1982, at Malham Cove).

The persistence of winter recharge may be seen to a lesser extent at other sites. The gradual depletion of $\delta^{18}O$ a Waterhouses (fig. 4.31(b)) from February to May, 1981, possibly reflects a lagged response to isotopically light precipitations in February and March. Additionally, the spring at West

Great Close, although similar in response to Waterhouses, tends to exhibit light $\delta^{18}O$ values for longer after input from winter recharge. This behaviour supports the earlier suggestion of the former catchment's receptiveness to winter precipitation; the memory effect indicates that complete homogenisation may not be occurring.

Information provided by the stable isotopes concerning the persistence of winter recharge contributes significantly towards the understanding of storage in karst hydrology; this evidence could not have been found using conventional hydrological methods.

(5) The fifth and final major feature of the monthly surface and groundwater results in the Malham area is the chemical and isotopic distinctiveness of the Tarn Outflow stream. Since this strongly influences results at the Airehead Springs, both sites will be considered here.

Both isotopic and chemical seasonal patterns of variation change dramatically in consideration of the Tarn Outflow water, in comparison with the waters which feed the Tarn. (eg. Waterhouses spring, which contributes an average of approximately 45% from month-by-month comparison of discharge at the two sites.) Minimum alkalinity, conductivity and Ca^{2+} occur in summer months at the Tarn Outflow, eg. 29 ppm Ca^{2+} in August 1982 in comparison with 83 ppm at Waterhouses for the corresponding month. Winter concentrations are, however, similar at output and input to the Tarn, eg. 61 and 63 ppm Ca^{2+} respectively in January 1982. The summer fall in carbonate concentrations is accompanied by a rise in pH. It may be attributed to the seasonal uptake of calcium carbonate by the aquatic organism Chara (PENTECOST, 1981). This was previously noted in examining the seasonal variation in $\delta^{13}C$; no influence is expected by this mechanism on the $\delta^{18}O$ concentrations (USDOWSKI et al., 1979).

Although water entering the wide and shallow Tarn has a fairly constant temperature of approximately 7.5°C, that leaving it displays distinct seasonal

variation, with range $0^{o}C$ to $18.7^{o}C$ over the period of study, reflecting the delay of water and opportunity for heat exchange in this upland lake. The pattern displayed in $\delta^{18}O$ is equally seasonal, with maxima in August/September. It appears to be quite independent (r=0.09) of discharge variations, which correspond closely with variations at the Waterhouses spring (r=0.76) and probably reflect the piston-flow mechanism of old water pushing out the new in the open Tarn. In tracing terms, a delay of approximately one month was seen of the actual water from input to output of the Tarn by examination of ^{3}H values (section 4.3.1(a)).

The $\delta^{18}O$ signal at the Tarn Outflow has been shown to be more strongly seasonal than that observed in precipitation, by a comparison of correlograms, in section 4.3.2(a). It is unlikely, that the Tarn Outflow water represents a smoothing of the average precipitation signal. Isotopic levels in the Tarn are heavier in summer months than those in precipitation, but never lighter in winter than the mean annual precipitation value. Additionally, the range of $\delta^{18}O$ values, from -7.7 to -5.7 $^{o}/oo$, is consistently above that of a mean baseflow value in the input springs. The possibility of summer isotopic enrichment in the Tarn was therefore explored, although at the outset of the study, such an effect had not been anticipated.

A $\delta^{18}O$-δD plot of samples from the Tarn Outflow was compared with monthly precipitation samples from Fountains Fell (fig. 4.44). Isotopically enriched summer Tarn samples appeared to fall on a line of lower gradient than that of precipitation. The overall gradient of the line for the Tarn water samples, however, was not found to be significantly different from that for precipitation; for the full data set at Tarn Outflow:-

$$\delta D = (5.27 \pm 0.56)\delta^{18}O + (10.77 \pm 3.92)$$

for n=27, r=0.88.

Unfortunately, when the data were split the small number of samples prevented statistical distinction of summer and winter gradients of $\delta^{18}O$-δD in Tarn

water. It is clear, however, that in qualitative terms isotopic enrichment relative to precipitation is seen to occur; continued sampling would be required to demonstrate the strength of this effect, but at least it has been shown to be a consistently seasonal effect.

An attempt was made to determine the amount of evaporation taking place from Malham Tarn. The Tarn was assumed to be a "lake of constant volume" after GAT (1981d) with rapid internal mixing relative to the residence time of water in the lake. The following equation was applied, therefore, from GAT & LEVY (1978):-

$$\frac{F_{in}}{E} = \frac{h}{1-h} \cdot \frac{\delta^{*} - \delta_{L}^{ss}}{\delta_{L}^{ss} - \delta_{in}} \qquad (4.1)$$

where $\delta^{*} = \frac{\varepsilon}{h} + \delta_{a}$, and is the limiting isotopic composition, of the lake on evaporation,

and F_{in} is the flux into lake and is equal to the flux out of lake (for constant volume)

E is the evaporation rate

h is relative humidity

δ_{in} is the isotopic composition of water entering the lake

δ_{L}^{ss} is the steady state isotopic composition of the lake

ε is the enrichment factor

and δ_{a} is the isotopic composition of atmospheric water vapour.

Values shown in table 4.30 were used in calculations of evaporation for February and July, 1981.

Assuming the Tarn (including peripheral sedge beds) to have an area of 0.7 km^2, evaporation rates calculated were 0.07 mm/day and 0.24 mm/day for February and July, 1981, respectively. These are of a reasonable order of magnitude (cf. potential evaporation in WARD, 1976) in consideration of the

data being used. δ_a in particular had to be estimated, no anticipation of the need for direct measurements having been feasible. Figure 4.45 shows a 10-fold variation in computed evaporation rates over a possible range of δ_a values. With further investigations of the parameters, however, water balance estimates of the Tarn may be made which would be difficult to derive directly by other means. This work would be of use in its application to reservoir waters in similar upland situations, as noted by BROWN et al. (1984a). Leakage from a reservoir could be identified by its distinctive seasonal signal; the Tarn water was clearly detected in this way at the Airehead springs.

Distinctive features of the hydrological and chemical plots (fig. 4.37(d)) at Airehead Spring (North) are (1) the discharge variations in almost direct agreement with those of the Tarn Outflow, its major feeder (r=0.87, n=23), (2) the subduing of the temperature regime of the Tarn-derived spring water (range $8^{o}C$ at Airehead), but which nonetheless is strongly seasonal, and (3) the modification of chemical composition of the Tarn waters at Airehead. The first feature reflects the strong connection between Water Sinks and Airehead, flow predominantly occurring in conduit passages, completely water filled in the synclinal section between Malham Cove and Airehead (section 3.2.1(d)). The latter two features reflect the transit of water through a limestone aquifer of relatively constant temperature, and the addition of fissure stored waters.

Measurements of conductivity, temperature and sampling for $\delta^{18}O$ at Airehead Spring South (figs. 4.38(c) and 4.33(c)) show values very similar to those at the more northerly spring. An exception is August 1982, when the southern spring still flowed, while the northern spring was dry; the flowing spring had high conductivity (326 $\mu S\ cm^{-1}$) and an isotopic compositon of -7.9 $^{o}/_{oo}$. The perennial nature of the southern spring is more probably due to its slightly lower altitude than to any major difference in conduit/diffuse flow contributions between the Airehead springs.

The $\delta^{18}O$ signal at Airehead is related to monthly chemical measurements only by the discrepancies between the Tarn Outflow waters and those at Airehead Springs being greatest at periods when the baseflow contribution is recognisable.

Initially it was considered that a simple mass balance could be carried out, assuming a constant baseflow contribution (δ_B) of say -7.8 °/oo, to compute the relative contribution of Tarn Outflow (Q_{TO}) water to Airehead Spring North (Q_{AH}), as compared with the discharge of baseflow (Q_B),:-

$$\delta_{AH}Q_{AH} = \delta_{TO}Q_{TO} + \delta_B Q_B \qquad (4.2)$$

Using this equation, 29% of flow at Airehead was computed to be baseflow in December 1981 (high flow) and 83% in May 1982 (low flow). This technique provides a useful indicator of relative contributions, where a positive connection has already been established (using artificial tracing) between two waters.

It is notable, however, that such a computation would produce erroneous values for Q_B where δ_{AH} is actually lighter than the assumed value of -7.8 °/oo, eg. when the observed Airehead value is -8.0 °/oo in April 1981. In such circumstances, it is assumed that the contribution from aquifer storage between Water Sinks and Airehead Springs is actually lighter than 'normal', possibly due to recharge by isotopically light winter precipitation over the relatively bare limestone between the Middle and North Craven Faults, as found previously at Malham Cove.

4.3.2(b) Lambourn area

Relationship between $\delta^{18}O$ in precipitation and in surface and groundwaters

In the correlation matrix of table 4.31 are the correlation coefficients (r) between precipitation in the month prior to sampling (using the composite

$\delta^{18}O$ series of Lechlade and Warren Down Farm data) and monthly values in ground and surface water. No sites show a significant correlation at the 95% level, and only Welford and Manor Farm have significant r values at the 90% level. These low correlations reflect the almost complete loss of a seasonal input signal in the waters sampled. In view of this, and the relatively long throughput times indicated by tritium levels, it was not considered useful to explore the $\delta^{18}O$ signals at a finer timescale. The possibility of occasional short-period responses will, however, be discussed in conjunction with chemical/hydrological data later in this section.

Relationship of $\delta^{18}O$ in surface and groundwaters, between sampling sites

The majority of relationships observed between $\delta^{18}O$ values at surface and groundwater sites in the Lambourn area are not strongly linear (table 4.31), although certain logical groupings of significant correlations do occur.

Correlation coefficients of 0.64 and 0.45 (significant at the 99% and 95% levels) are found between $\delta^{18}O$ at the source of the River Lambourn and its upper catchment boreholes at Ashdown Park and Oakash borehole respectively. Oakash also correlates significantly with $\delta^{18}O$ at Bagnor, to which it may also contribute. Bagnor, in turn, exhibits the highest correlation coefficient (0.76) with water of the River Lambourn at Shaw, possibly indicating the importance of groundwaters with a similar history (and isotopic composition) to those emerging above Bagnor, in contributing to flow at Shaw. The intermediate site on the River Lambourn, at Welford, shows very low correlations with the other sites, but it is possible that, in this area, only slight variations (within measurement error) may strongly affect the linearity of relationships between the series under examination.

The small number of samples and the possible dominance of borehole flooding at North Farm (in February and April 1982) may account for the low correlations found between this borehole and other sites in the area.

It is apparent that Manor Farm borehole waters do not vary directly with

River Lambourn waters (r values range from 0.05 to 0.31), despite the borehole's proximity to the river and its valley bottom location in (relatively high transmissivity) river gravels. This relationship will be examined further in conjunction with hydrological measurements and chemical analyses.

Relationship between $\delta^{18}O$ in surface and groundwaters with conventional hydrological measurements

The only variables which exibit significant linear correlation at the 95% level with monthly $\delta^{18}O$ values (table 4.32) are alkalinity at Manor Farm borehole and Ca^{2+} at Ashdown Park borehole. Both relationships are inverse (r values -0.58 and -0.84 respectively). The lack of distinct correlations illustrates at least that $\delta^{18}O$ is not duplicating information provided by other variables, which may be simpler and/or cheaper to measure. In order to interpret the small $\delta^{18}O$ variations observed, however, we must consider them in conjunction with conventional hydrological data.

The main features of the Lambourn area $\delta^{18}O$ deviations away from mean values (fig 4.32 and section 4.3.1(b)) may be listed as:-

(1) A positive deviation from mean values in October/November 1981 at all sites.

(2) A negative deviation in river waters in October/November 1982.

(3) Positive deviations in May/June and June/July 1981 at Ashdown Park/Oakash and at Shaw respectively.

Events (1) and (2) occur at low flows and low free water table levels in the catchment, and do not appear to reflect a runoff response. Precipitation $\delta^{18}O$ values in the preceeding months are respectively more negative and more positive than the mean surface/groundwater values (ie. deviations in input are in opposite directions to those measured in surface and groundwaters). Higher alkalinities are generally found in the lower discharge conditions and larger deviations from mean surface water temperatures occur in the slow

moving water. In-channel processes, however, are not expected to be responsible for these deviations. Interestingly, the peak in $\delta^{18}O$ (case (1)) is found to occur one month earlier in borehole waters, except for Ashdown Park, relative to river waters, in 1981, ie. in October as compared with November. The lag of the river water behind water sampled at Manor Farm borehole indicates that, at this time of the year, flow is in a predominantly river-ward direction, with a time of travel of approximately one month between the point of interception in Upper Chalk at the borehole, and the point of discharge into the River Lambourn.

A similar lag is found in case (3) (above) in river waters in June/July 1981 as compared with the positive deviations in $\delta^{18}O$ at Ashdown and Oakash in May, these coinciding with a period of high water levels and generally low conductivity, alkalinity and Ca^{2+} concentrations.

Unfortunately, inadequate borehole data are available for comparison with river waters in October/November 1982 (case (2)), in low flows; the isotopic deviation is relatively small. It is important to note, however, that the direction of deviation is opposite to that found in the corresponding dry period of 1981. A simple relationship between water table level and $\delta^{18}O$ may not therefore be expected. More detailed chemical information is ideally required (eg. of trace elements and chemical assemblages particular to specific lithological horizons, and found in the waters issuing therefrom) to identify the sources of river flow in high and low discharge conditions; this is a problem which, due to relative homogeneity in concentrations, $\delta^{18}O$ determinations do not appear to contribute a great deal of information.

The occurrence of $\delta^{18}O$ variations with depth in a saturated aquifer found in the depth sampling of section 4.3.1(b) neither verifies nor falsifies the occurrence of by-pass fissure flow in the unsaturated zone. There is a danger, however, in isotopic variations in river waters being falsely interpreted as being due to recent precipitation input where the saturated

groundwater source is not itself homogeneous. A flashy but not direct (eg. pressure induced) response to a rainfall event may produce isotopic variation by the combined contribution of non-homogeneous groundwater into springs feeding the river. The riparian direct input mechanism of GASQUOINE (1978), section 3.2.2(d), need not be invoked, but is equally not disproven using the isotope technique.

Through the monitoring period, only one sampling date was found to correspond closely with an incident of river discharge 'flashiness', on 22.7.1981. A response to relatively high daily precipitation totals (3.5 and 6.1 mm on the 21st and 22nd respectively) was the apparent cause. This was the first substantial rain since early June (WEATHER, 1981). Air flow was from a northerly direction on the 22nd, as a depression tracked south-east over the U.K. Precipitation derived therefrom was isotopically heavy, with $\delta^{18}O$ value -3.8 $^{o}/_{oo}$ recorded for the weekly sample from Lechlade. Responses in stage at East Shefford, Welford and Bagnor are shown in fig. 4.46. No isotopic response, however, is found at these locations, all river waters lying within experimental error of the mean, -7.5 $^{o}/_{oo}$. The operation of fishery sluices and minor pumping tests in the catchment may account for, or at least contribute towards, the higher isotopic variability at the most downstream site at Shaw. If this were the case, however, a better correspondence of $\delta^{18}O$ with conventional hydrological indicators would be expected. $\delta^{18}O$ data are inadequate to differentiate such events from the possibility of increased downstream direct runoff over Tertiary beds (and possibly through connecting and solutionally widened fissures) into river waters. More detailed monitoring and/or artificial tracing studies would be required to explore this hypothesis.

4.4 Results from sampling soil moisture and cave drips

Soil moisture sampling results will be reported from both the Malham and the Lambourn areas. Cave drips were collected in the Malham area only.

4.4.1 Soil moisture

Isotopic results of suction cup extractions of soil moisture are shown in fig. 4.47 (Knowe Fell/Turf Hill, Malham area) and fig. 4.48 (Manor Farm, Lambourn area). Sampler efficiency at both locations was variable through the year, and partly dependent for 'day of visit' samples upon the time over which suction was applied (between 0.2 and 2.2 hours).

For the Malham area, figs 4.47 (b) and (c) show a significant range of $\delta^{18}O$ variations, for samples taken on the day of visit and over one month, respectively. The volumes of sample collected were more erratic in these soils which were more frequently unsaturated, and less homogeneous than the peats of the Lambourn area.

The observed range in $\delta^{18}O$ (Malham area) is from -7.9 to -5.5 $^{o}/_{oo}$, with mean of -6.9 $^{o}/_{oo}$ for all samples (n=30, σ=0.6 $^{o}/_{oo}$), ie. significantly heavier than mean weighted precipitation values. From the evidence of heavy isotope retention at high tensions found experimentally in section 3.5.4, it may have been expected to obtain generally higher $\delta^{18}O$ values on the day of sampling, as compared with samples entering the suction cup over a period of one month; the latter have ample opportunity for exchange with isotopically lighter water in periods of low tension, especially near saturation or field capacity, when water may freely enter and leave the pot. On only one occasion is this observed, however, for sampler THD in February 1982 (with sampling day value of -5.5 and monthly value for January of -7.3 $^{o}/_{oo}$). On other occasions, a close match between daily and monthly values is observed, or else the monthly sample is isotopically heavier. No evidence, however, of significant kinetic evaporation was found in either category of soil moisture sample (see $\delta^{18}O$-δD plot, fig. 4.34).

The suction cup samplers each appear to behave in a slightly different manner. $\delta^{18}O$ values from THC (at 80 cm) and the Knowe Fell sampler (installed for four months only at 50 cm in peat) both show relatively small variations. Intermediate (except for February 1982) variations are found with THD, at 70 cm, and the largest variations are found with the shallowest sampler, THE at 35 cm. Decreasing isotopic variability of mobile water with depth, in the context of the hillside peaty podsol of the Malham area may indicate:-

(1) downward mixing and delay of waters recharging the limestone below; and/or

(2) higher throughflow rates (predominantly lateral flow), accompanied by less mixing and storage in upper soil horizons which exhibit a more granular structure and higher transmissivity.

In view of the high clay content and relatively impermeable nature of the drift C horizon, the second option is favoured.

Re-examination of fig. 4.47(c) shows isotopically heavier soil moisture to be found in winter months, eg. in December 1981 (for THE) and lighter values in summer. Thus a lag of 3-6 months is apparent relative to the general pattern of isotopic variation in precipitation. Such an observation, although tentative in this study is important; it contributes towards locating the position in the hydrological cycle where smoothing of the isotopic input signal occurs.

Retention and slow transmission of water by soils provides effective initial mixing of the stable isotope signal. Subsequent displacement of this water, eg. by piston flow, with possible transmission into fissures and/or pipes (in soil or limestone bedrock) would be expected to give an isotopic response unrelated to the recent precipitation input values. Only by direct input of precipitation to the system, with by-pass flow, or by inhomogeneous storage of water in enclosed pockets which are subsequently released, may

isotopic variations be expected from a limestone area with a thick soil cover.

In the Lambourn area, samples from Manor Farm water meadow are presented in fig. 4.48. Values are shown for the day of visit only; this normally provided sufficient sample for $\delta^{18}O$ measurement. $\delta^{18}O$ values (mean -7.0 $^{o}/_{oo}$ from 8 soil moisture analyses) are heavier than expected from consideration of precipitation input. Variations do appear to follow a weak seasonal pattern, and fig. 4.34 has already shown there to be no consistent trend attributable to the suction cup technique in the $\delta^{18}O$-δD away from a relationship similar to the Meteoric Water Line, which would be due to kinetic evaporation. Although most probably derived from chalk groundwater and/or river waters, no clear relationship exists between $\delta^{18}O$ in and these waters and soil moisture; with so few samples, and $\delta^{18}O$ variations in the chalk area commonly occurring within experimental error, evidence of a statistical relationship would not, necessarily imply a causal link.

The limited range of $\delta^{18}O$ values (-7.2 to -6.7 $^{o}/_{oo}$) may be attributed to either a damping effect before input of water to the meadow and/or damping of precipitation input by the soil. The mechanism by which a shift in mean $\delta^{18}O$ is produced requires further study, for example by an investigation into water uptake and evapotranspiration by vegetation with respect to isotope 'seasons' in precipitation. The isotopic shift may be important in hydrological terms since the mobile water draining from the meadow areas (forming approximately 1% of total Lambourn catchment area), eg. in the recession of the water table in October/November, might be expected to contribute isotopically enriched soil moisture to the river, this forming a useful label of water source.

4.4.2 Cave drips

$\delta^{18}O$ analysis results of monthly accumulated cave drips, collected beneath bare limestone, are given in fig. 4.49. The number of samples presented are few due to occasional months where poor positioning of the collector caused no drips to be received, and due to the limitations of time

available for analysis. Overflow of the collection vessel additionally occurred on six occasions.

$\delta^{18}O$ variations observed correlate at the 99% level of significance with monthly precipitation at Fountains Fell (r=0.78, n=13, table 4.27). No consistent modification of $\delta^{18}O$ relative to precipitation is observed and the range of values is similar. It appears that the absence of a soil cover and the shallow depth of limestone (3 m) above Chapel Cave provide little or no opportunity for mixing and storage of water at the timescale of one month. This does not imply, however, that mixing of precipitation may not occur in the unsaturated zone of limestone below bare pavement, eg. in an epikarstic zone, in the Malham area, where aquifer depths of up to 200 m may be found. Unfortunately, no caves in the Malham area have yet been discovered which could provide drip samples at depth; isotopic evidence is required from comparable areas of bare horizontal karst, with more permanent and more detailed drip collection (eg. over storm events) and in conjuction with conventional dye tracing. Such experiments have been carried out by Atkinson and others in the Mendip Hills, Somerset (T.C. Atkinson, written pers. comm. 1981), and more significantly in the region of White Scar Cave, North Yorkshire (ATKINSON et al., 1984).

The latter detailed investigation of karst recharge processes complements well the present, relatively long-term, study. Preliminary results indicate drips and flows to have variable behaviour. Some have constant isotopic composition, indicating already well-mixed sources. Others show variations from a few per cent up to almost half of the range observed in precipitation, with a time lag of up to two months.

4.5 Results of storm sampling, Malham area

4.5.1 Short period isotopic variations

Evidence of short period isotopic variations in surface waters of the Malham area was provided by analyses of samples taken on consecutive days. The most extreme event sampled in this way occurred on 2.1.1982 and coincided with snowmelt. $\delta^{18}O$ at Waterhouses spring fell from -8.1 on the day of routine sampling, to -9.2 $^{o}/oo$ after snowmelt on 3.1.1982. The corresponding drop at Airehead Spring (North) was from -7.7 to -8.5 $^{o}/oo$, accompanied by a rise in discharge of 0.54 m^3s^{-1}. Almost complete isotopic recovery was apparent at this site, on 4.1.1982, when a $\delta^{18}O$ sample of -7.9 $^{o}/oo$ was collected. A limited number of repeat samples taken in the Malham area over smaller events (31.1.1982 and 1.4.1982) exhibited no significant change in isotope levels. A second attempt was made to intercept a snowmelt event in February 1983, full details of which for sampling at Waterhouses will be presented in the next section. In the same event, constituting predominantly the recession limb of a hydrograph, $\delta^{18}O$ values at Airehead Spring (North) rose from -7.9 (1.2.1983), through -7.6 (2.2.1983) to -7.5 $^{o}/oo$ (5.2.1983). Interestingly, initial values at the southern Airehead spring had been lower, at -8.1, rising to -7.8 $^{o}/oo$ on 2.2.1983, indicating a slightly greater proportional contribution of isotopically light (snowmelt) input at the smaller spring. $\delta^{18}O$ at the Tarn Outlfow was -7.5 $^{o}/oo$ throughout. The response at Malham Cove was the most dramatic, from -8.9 on 1.2.1983, through -8.2 (2.2.1983) to -7.8 $^{o}/oo$ (5.2.1983), reflecting, perhaps, the importance of snowmelt over a wide area of bare or patchily covered limestone between the Middle and North Craven Faults. More negative $\delta^{18}O$ values were observed at the Cove than found in Smelt Mill sinking stream, its only proven discrete and allogenic input.

The above examples illustrate the degree of isotopic variance, of the

order of at least ± 1.0 °/oo in $\delta^{18}O$, which may remain unobserved using the method of monthly spot sampling.

4.5.2 Storm sampling at Waterhouses Spring

Seven series of sampling during rainfall/snowmelt events were carried out, in total, at Waterhouses Spring. One series was of baseflow (from 4.9.1981 to 6.9.1981) with no rainfall during the time of sampling, and exhibited no significant variations in δD (all at -50 ± 1 °/oo) over a 66 hour period of two-hourly sampling. Minor storm events, one in September 1981 and two in April 1982, with respective rainfall input totals of 17.8, 3.7 and 11.9 mm (of which 0.9, 0.3 and 0.5 mm were effective), produced little or no response in discharge at Waterhouses. Chemical parameters did not vary beyond measurement error, and isotope analyses were not undertaken. Precipitation input and hydrological, chemical and isotope responses are, however, presented for hydrograph events in October 1981 (figs. 4.50, 4.51, 4.52), November 1981 (figs. 4.53, 4.54 and 4.55) and Feburary 1983 (fig. 4.56). Stream sampling took place at two-hourly intervals, except in February 1983 when intermittent equipment failure (partly due to freezing conditions) resulted in irregular manual sampling. $\delta^{18}O$ measurements were made only on 6 hourly samples for the November series in view of the small variations observed. Unfortunately the autographic rainfall recorder at Malham Tarn Field Centre meteorological station was not working for the period of the first two events reported.

Results from each of the three storms will be examined in turn, followed by some general comments regarding the pattern of results.

October 1981

(Sampling starts at 20:30G.M.T., 30.9.1981)

An example of the short-period response of Waterhouses Spring to storm rainfall is shown in figs. 4.50, 4.51, and 4.52. The curves of conductivity and Ca^{2+} concentrations (fig. 4.52) are characterised by a slight increase at the onset of the hydrograph response, (fig. 4.50) possibly due to displacement

of fissure storage, followed by dilution curves which correspond to the two discharge peaks.

The response in $\delta^{18}O$ values, shown in fig. 4.51, is less marked, hardly exceeding experimental errors for many samples, and is more difficult to explain. From 0 to 23 hours after the start of sampling, 51 mm of rain fell with average $\delta^{18}O$ of -6.1 °/oo, ie. isotopically heavier than the initial spring water which was at -7.5 °/oo. An isotopic response to this might have been expected at the spring, but is not clearly seen over the observation period. It is noted that isotope values relating to the initial rising limb of the hydrograph are erratic. From 23 to 38 hours, the average input of -7.2 °/oo in 14.3 mm rainfall is probably too close to baseflow values to be detectable. However, from 36 to 62 hours, a very light isotopic input of -17.6 °/oo in 14.7 mm might account for the falling isotope levels in the spring, approximately 40 hours later, towards the very end of the observation period. The interpretation is made more difficult because the rainfall averages apply only to a single collection point, whereas stream water is derived from a wide area, and also the stream samples are spot measurements, not weighted for discharge amounts.

A possible explanation of the lack of $\delta^{18}O$ variation at the spring is that the water undergoes a complexity of mixing and displacement in the catchment area. This may take place in a zone in the aquifer above that where preferential flow paths are evidenced by the response of chemical parameters, which are more dependent upon process dynamics. MEROT et al. (1981) similarly found hidden complexity in hydrograph response after analysis for stable isotopes and attributed this, in non-karst area, to releases from different hydrological reservoirs. This type of multi-reservoir behaviour has previously been difficult to define at karstic resurgences, ie. the classification represents a grey area in the schema of fig. 1.6(a).

The extent of the averaging effects in the aquifer is unexpected and

demonstrates the power of the isotope technique in providing information which could not be obtained by conventional hydrological methods.

November 1981

(Sampling starts at 17:30 G.M.T., 28.10.1981)

Only 12.5 mm of rainfall fell over the period of sampling, and the response in discharge is correspondingly small (fig. 4.53), with maximum value 0.63 $m^3 s^{-1}$ after 36 hours of sampling; before this, a series of minor peaks are seen in the hydrograph. The discharge maxima correspond with the Ca^{2+} and conductivity minima (fig. 4.55). $\delta^{18}O$ values in precipitation (fig. 4.54(a)) are heavier, at -2.3 to -4.1 $^{o}/oo$, than the initial baseflow value of -7.5 $^{o}/oo$ at Waterhouses (fig. 4.54(b)). Interestingly, the baseflow value appears to drop to -7.8 $^{o}/oo$ on the recession curve. Initial variations of $\delta^{18}O$, during the rising limb, are all within experimental error, and correspond with minor rises in Ca^{2+} and conductivity. A major rise in $\delta^{18}O$ is seen, however, between 30 hours (-7.8 $^{o}/oo$) and 36 hours (-7.5 $^{o}/oo$) which corresponds with the maximum dilution period in chemical parameters. It is possible that this water includes some of the isotopically heavy recent precipitation, which is diluted by the lighter mix of water in fissure storage. It appears that the heavier water continues to contribute to the Waterhouses Spring in the recession limb of the hydrograph. Interpretation remains tentative, however, in view of the small variations observed in the whole series, relative to experimental error. It is possible that the sampling period was too short to have observed the full response of the spring to the measured isotopic input, and that future studies should employ more extended storm sampling.

February 1983

(Sampling starts at 15:10 G.M.T., 1.2.1983).

Discharge during the recession limb of the hydrograph sampled falls from 0.64 $m^3 s^{-1}$ to 0.04 $m^3 s^{-1}$, and is accompanied by a general rise in Ca^{2+} concentrations and in conductivity (fig. 4.56). Snowmelt was the cause of the

hydrograph rise, and sampling of fresh snow and of snow cores gave $\delta^{18}O$ values of the snow in the range -9.6 to -12.7, with mean -11.6 °/oo (7 samples). Snow equivalent to 30 mm of precipitation had fallen between 29.1.1983 and 1.2.1983 in the Malham area. The initial low $\delta^{18}O$ value observed at Waterhouses Spring, of -9.0 °/oo, was evidently in response to the snowmelt. Recovery of $\delta^{18}O$ values occurs only to -8.6 °/oo after 54 hours. Continued sampling of the recession may have shown further increases in $\delta^{18}O$, although seasonal (monthly) sampling in the Malham area has indicated that the impact of isotopically distinct snowmelt in significant quantities may persist in baseflow for several months under certain conditions. The isotopic variations about -8.5 °/oo after 50 hours of sampling indicate that the source of water contributing to baseflow was not totally homogenised.

General comments

Short period $\delta^{18}O$ variations observed at Waterhouses Spring were subdued in comparison with those in precipitation input and also with those variations observed on a seasonal basis. Snowmelt appeared to exhibit the greatest isotopic impact on these waters. Considerable delay and mixing of input waters was apparent in storm sampling of stable isotopes; this contrasts with chemical parameters which frequently showed clear dilution effects which would normally be interpreted as the contribution of recent rainfall to the system. Although this may in certain cases be true (eg. in November 1981), it is apparent that water contributing to spring flow is more well mixed, although not necessarily homogenised, than previously appreciated using conventional hydrological techniques.

PART 5 CONCLUSIONS AND RECOMMENDATIONS FOR FUTURE STUDIES

5.1 Conclusions

A monthly programme of precipitation, and ground and surface water monitoring for stable isotopes was successfully carried out over a two year period in two contrasting study areas in the U.K. Sampling of intermediate stages of the hydrological system and more intensive monitoring of isotope variability also took place. The major conclusions of the study will be presented in accordance with the objectives listed in section 1.2. Conclusions are additionally drawn of experimental work investigating sampling methods; the methods developed and tested are an important contribution of this study. Finally, the study will be assessed in terms of the degree to which it achieves its overall aim.

Precipitation

1. The stable isotope signal monitored in monthly precipitation at stations in each of N.W. Yorkshire, Berkshire and Oxfordshire was found to exhibit variations which were definable well beyond measurement error. The observed $\delta^{18}O$ range of 10 $^{o}/_{oo}$ represents approximately one hundred times that error ($\pm$0.1 $^{o}/_{oo}$ at 1σ). Correlogram analysis showed that the signal in the U.K. was less strongly seasonal, and more erratic, than that found, for example, by YURTSEVER & GAT (1981) in precipitation over continental Vienna. In Malham, variations were detected in weekly precipitation which had remained unobserved in monthly collections; these introduced a larger range in $\delta^{18}O$ (a total of 15 $^{o}/_{oo}$) and additional 'noise' into the signal. Further $\delta^{18}O$ variations were detected in within-storm sampling, but these had a relatively small range (a mean of 6.5 $^{o}/_{oo}$ in this study). It is concluded

that at each timescale investigated, a clear stable isotope input signal is available in the U.K. and is therefore potentially of use for natural hydrological tracing studies.

2. Investigations into the meteorological isotope 'effects' at both monthly and weekly timescales, showed that the $\delta^{18}O$ values measured in precipitation were not strongly sensitive to precipitation amount (P, mm) or to air temperature (T, ^{o}C). The following relationships were found at Malham Tarn Field Centre:-

Monthly: $\delta^{18}O = (-8.87 \pm 0.39) + (0.18 \pm 0.05)T$ [r=0.58, n=27]

$\delta^{18}O = (-6.01 \pm 0.44) - (0.012 \pm 0.003)P$ [r=-0.66, n=27]

Weekly: $\delta^{18}O = (-9.43 \pm 0.40) + (0.28 \pm 0.05)T$ [r=0.50, n=100]

$\delta^{18}O = (-6.17 \pm 0.40) - (0.039 \pm 0.009)P$ [r=-0.39, n=100]

The regressions are significantly linear at the 95% level of confidence, but levels of explained variance are low. In the U.K., it appears that reliable explanations or predictions of isotopic inputs for natural tracing studies cannot be made using solely these meteorological parameters.

3. The characterisation by air mass of weekly isotopic input did not significantly improve the explanation of the $\delta^{18}O$ variations. Certain general patterns emerged from this investigation, however, which may be useful for future studies. It was found that westerly and north-westerly circulations generally produce isotopically heavy

rainfall, probably due to their initial rainout occurring over the U.K.; cyclonic circulations bring already depleted precipitation; rainfall from anticyclonic circulations is isotopically heavy and generally associated with warm conditions. Precipitation from other circulations exhibits considerable variability in $\delta^{18}O$, often dependent upon the season, and accordingly is less reliable in terms of its potential for natural tracing.

A search was made for alternative meteorological indicators of strong deviations in isotopic input. Snow was found to be frequently isotopically distinct (light) and it is suggested that snowmelt provides the most reliable natural tracer 'spike' in the U.K. At the within-storm timescale, occluded fronts appear to provide the most reliable and distinct isotope tracer; rainfall so produced was found to be strongly depleted in $\delta^{18}O$.

5. No significant altitude effect was found over the range of 472 m available in the Malham area, in monthly precipitation samples. An overall (unweighted) effect in $\delta^{18}O$ of 0.05 ± 0.39 $^{o}/_{oo}$/472 m was measured; this indicates a slight isotopic enrichment with altitude, ie. an altitude effect in the opposite direction to that anticipated. Separating out the summer months, a maximum depletion of -0.26 ± 0.16 $^{o}/_{oo}$/100 m was detected, which agrees well with isotopic projections made from reports of lapse rates in the Northern Pennines by MANLEY (1943); the average summer effect, however, was only -0.11 ± 0.13 $^{o}/_{oo}$/100 m. The overall effect is weak and unreliable in comparison with those effects measured and applied in hydrological tracing studies elsewhere. The isotopic altitude effect in the U.K. is expected to be of no practical value for natural tracing, and in the majority of studies at the catchment scale or less may be ignored.

6. The $\delta^{18}O$-δD relationship of monthly precipitation was found to have a gradient similar to that of the Meteoric Water Line (CRAIG, 196la), but a lower intercept value. This was as expected for a mid-latitude station according to data of the IAEA-WMO monitoring network (section 2.3.2(c)). The relationship computed for Malham Village/Malham Tarn Field Centre precipitation was:-

$$\delta D = (7.22 \pm 0.51)\delta^{18}O + (3.10 \pm 3.85) \qquad [r=0.95.\ n=23]$$

The identification of this regression line provides a useful data base for studies investigating evidence of isotopic alteration in natural waters in the U.K.

Surface and groundwater

7. Surface waters in the Malham area exhibited significant isotope variations whereas $\delta^{18}O$ levels in Lambourn area surface waters were relatively invariant and generally close to the weighted mean value in precipitation. Input signal attenuation of 57% and 88% in waters of the respective areas was observed, as measured by the reduction of the $\delta^{18}O$ range in surface waters relative to the range in precipitation. The greatest hydrological information was available in the stable isotope data from sites where significant $\delta^{18}O$ variations were observed, notably in the Malham area. Variations in the Lambourn area of chalk, which rarely exceeded measurement error, showed the water to be well mixed over a period of one year or more. Variations in tritium of the water, however, indicated that complete homogenisation of the chalk water does not occur. It appears that the future use of the stable isotope technique in U.K. chalk hydrology may be limited to studies of recharge dynamics in the unsaturated zone, during which total smoothing of the input signal occurs.

8. Groundwater sampled from boreholes in the Malham and the Lambourn areas was remarkably invariant in its isotopic composition, and in both areas was close to mean values in precipitation. The groundwater sampled was predominantly derived from fissure and diffuse flow, in the two areas repsectively; the opportunity for mixing and delay in transmission of this water was great, and the lack of isotopic variance was not surprising. No stable isotope evidence was found in the chalk waters of rapid by-pass flow through the unsaturated zone to the water table, but this does not disprove the existence of the mechanism, since the water so transmitted may already be isotopically well mixed. An apparent spatial pattern in $\delta^{18}O$ was detected in Lambourn area groundwaters, but its explanation required further study.

Soil moisture and cave drips

9. A reduction of 74% was found in the total $\delta^{18}O$ range in Malham soil moisture relative to the range in monthly precipitation. Attenuation of the input signal increased with depth. The degree of attenuation was surprising. Where isotope input signals are relatively weak, as in the U.K., proper assessment of soil cover is essential in the choice of study area, even if hydrogeological transmission times are known to be fast, so that research design may accommodate this important source of signal damping.

The reduction of input signal $\delta^{18}O$ range in the Lambourn soils was 95% relative to precipitation input. This high degree of damping was not surprising since soil moisture in the water meadow was considered to derive principally from (isotopically invariant) chalk groundwater and/or chalk river water.

10. Cave drips in this study (from Chapel Cave, Malham area) were sampled too close to the surface to have undergone any significant processes of subcutaneous mixing and storage; $\delta^{18}O$ values in drips were not found to be significantly different from those in the corresponding months of precipitation.

Comparison with conventional hydrological data

11. In certain cases, $\delta^{18}O$ data confirmed hydrological behaviour which was evident from conventional data. In the Malham area, characteristic baseflow $\delta^{18}O$ values were indentifiable. These were close to mean annual values in precipitation and were associated with characteristic chemical compositions in the water; such evidence of well-mixed fissure storage may be anticipated from both traditional and more recent subcutaneous models of karstic aquifer behaviour (eg. of ATKINSON, 1971, and of WILLIAMS, 1983, respectively). In high flows, both isotopic deviations from baseflow values and chemical dilution effects indicated the arrival of 'recent' input waters. Knowe Fell sinking stream was very responsive in this manner; it exhibited the highest correlation of all sites between $\delta^{18}O$ and a conventional hydrological measurement (correlation with discharge, r=-0.83).

An advantage of the baseflow $\delta^{18}O$ values is that, due to the conservative properties of the isotope as a tracer, it may be used in simple mass balance calculations. This is possible in cases where additional input isotopic values are known. Examples of applications in this study are hydrograph examination (at Waterhouses Spring) and sink-resurgence analysis (performed for the Tarn Outflow-Airehead springs system).

12. Stable isotope determinations have also provided evidence of processes not observed by other methods. The apparent persistence of winter recharge into summer baseflow is such a process. It was seen to occur in the linked system of Smelt Mill sink feeding Malham Cove spring and was identified by the large and subsequently decreasing $\delta^{18}O$ difference between the sites, after periods of isotopically light input. This memory effect in the aquifer lasted for 3-4 months. It also occurred at other sites where the diffuse component of flow was high; and also where recharge was through limestone pavement with only a thin soil cover, for example, at West Great Close spring. The mechanism for the incomplete mixing is not clear from this study; it may occur in a temporary storage zone in the upper aquifer (ie. a subcutaneous reservoir) which subsequently drains, by-passing a deeper more well-mixed reservoir.

13. In surface waters of the Malham area, short period isotopic response was greatest to snowmelt events. In such periods, individual error bars of at least $\pm$ 1.0 $^{o}/_{oo}$ in $\delta^{18}O$ were apparent where single spot sampling at a site was taken to represent isotopic conditions over the sampling month. Springs fed by snowmelt over the area of relatively bare karst between the North and Middle Craven Faults were particularly isotopically responsive, indicating flow paths in which mixing with reservoir storage was minimal. In contrast, isotopic variations during rain-storm hydrographs at Waterhouses spring frequently did not exceed experimental measurement error. This isotopic constancy accompanied carbonate chemical dilution effects at the spring, after displacement of (more highly concentrated) fissure storage. It appeared that the 'recent' water, responsible for the dilution, is in fact already well mixed at the scale of isotopic input variations. Significantly, a zone

of mixing and storage is indicated to exist above that one in which chemical dissolution processes predominantly operate. This type of multi-reservoir behaviour has previously been difficult to define at resurgences, using chemical information alone.

14. The stable isotope signal at the Tarn Outflow was found to be more strongly seasonal than that in precipitation. Poor correlations of $\delta^{18}O$ in input waters to the Tarn with the precipitation signal discounted the hypothesis that a smoothing of the precipitation signal was being observed. Isotopic levels in the Tarn were heavier in summer months than those in precipitation, but never lighter in winter than the mean annual precipitation value. Calcium carbonate precipitation by Chara in the Tarn (PENTECOST, 1981) was rejected as the driving force of the $\delta^{18}O$ variations on the evidence of experimental work by USDOWSKI et al. (1979). These observations and arguments led to the proposal that isotopic enrichment of the water occurred in its passage through the wide and shallow Tarn; throughput times of the order of one month were apparent from comparisons of tritium measurements at an input spring with concentrations at the Tarn Outflow. A $\delta^{18}O$-δD plot of the Tarn Outflow water, however, showed no statistically significant difference from the regression of precipitation, but evaporation was inferred from the consistency of isotopic shifts in the limited number of samples (n=27). A calculation was attempted to determine the open-water evaporation rates from the stable isotope data using the method of GAT & LEVY (1978). Results were plausible but strongly dependent upon values which had not been measured over the study period. The fortuitous discovery of this distinctive isotopic signal provides considerable potential for further research and future applications using the stable isotopes in the U.K.

Experimental developments in method

15. The last conclusion refers not to the results of the main hydrological study, but to experimental investigations into sampling methods. The use of a silicone oil film was found to be an effective suppressant of evaporation from water samples, under laboratory conditions; displacement or dispersion of the film, however, rendered it ineffective. Comparisons were made of $\delta^{18}O$ in precipitation using collectors with and without the use of an oil film. It is concluded that the use of the oil film is unnecessary in the U.K. if a Bradford or Octapent style of raingauge is used as a collector. Other collector styles appear to require the continued use of an oil film. A standard style raingauge with adequate exposure is preferred for the reliability of its catch. At Malham Tarn Field Centre, using a pair of such raingauges, isotopic ($\delta^{18}O$) agreement was normally found to be within experimental measurement error.

For stable isotope measurement of separate snow samples, the procedure of enclosed melt used in this study is recommended in preference to open dish melt procedures; using the latter method considerable isotopic alteration was found to take place.

In situ suction cup extraction of soil moisture was found to yield isotopic results significantly lighter (by up to 3.3 $^{o}/_{oo}$ in $\delta^{18}O$) than soil moisture extracted by the three alternative methods investigated (centrifuge extraction by drainage and by displacement, and vacuum distillation). This difference was attributed to the removal by the alternative methods of tightly bound water (at tensions of between 1.0×10^5 Pa and 31.4×10^5 Pa), which was found to be isotopically heavier. The method of low tension extraction is considered both suitable and convenient for studies where the monitoring of mobile water in recharge processes is of prime importance.

5.2 Recommendations for future studies

Several recommendations arise from this study and proposals are made both for (a) further experimental and field investigations, and (b) direct practical applications of the stable isotope technique in the U.K. In general, it is important that future studies choose a scale of investigation and degree of probable water mixing, which is appropriate to the input signal variations which have been shown to be available, in the U.K.

Experimental and field investigations

1. Better understanding of the isotopic input signal in precipitation in the U.K. would give a firmer base to studies using the stable isotopes as natural tracers. At present it is essential that the input signal be monitored at an appropriate sampling interval and close to, if not within, the study area. With improved power of explanation, probable isotopic input could be specified for periods or areas where actual isotopic data did not exist. Additionally, predictions of isotopic input from synoptic forecasts would enhance the prospects for successful storm studies in quick response systems, and make their operation more efficient. The air mass classification approach, employed in this study gave encouraging results. An extension of this work would be to incorporate into a regression model the physically meaningful parameters which characterise the air masses; examples are previous rainout amounts and typical condensation temperatures, possibly allowing for seasonal variations in these parameters. Close collaboration with meteorologists and/or synoptic climatologists is required for the link to be made between purely statistical relationships with isotopic signals and the physical processes contained therein.

2. The need for further investigations into the attenuation of input signals in soils is highlighted by this study, since over half the original range of isotopic input may be lost in this zone. A geomorphological approach would be beneficial. In an area such as Turf Hill (Malham), for example, it is anticipated that each process of overland flow, infiltration and throughflow be accompanied by different degrees of mixing and storage. Geographical variations in the balance of processes will depend upon both pedological controls and morphological features. Intensive instrumentation and isotope monitoring, at the scale of the hillslope would assist not only in the general advancement of the stable isotope technique, but also in solving existing controversies in soil physics (eg. by defining the degree of previous mixing in macropore flow, using the natural tracing properties of the isotopes).

3. A very promising area for the use of stable isotopes is in the examination of mixing and storage in the vadose (unsaturated) zone of the karstic aquifer. Studies of stable isotopes in cave drips in the U.K., in the absence of strong seasonality or altitudinal effects, require more careful sampling programmes and demand a knowledge of percolation flow paths from conventional tracing methods; such studies have been initiated by Atkinson and others in N. Yorkshire. It is suggested from the present study that investigation of recharge processes below bare karst and below soil covered surfaces could contribute significantly to the understanding of responsivity to, and persistence of, isotopically light winter recharge, at certain resurgences.

4. It was unfortunate in this study that inadequate time was available for full chemical analyses of the waters sampled. Discrimination of a range of resurgence flow regimes according to isotopic attenuation of input signal and to chemical variability could form the objective of a further study. Chemical parameters to be investigated would be those describing the evolution of the water, eg. pCO_2 and SI_c. Such a study need not be limited by geographical area, and would ideally use a combination of 'classic' sites (eg. including waters from the Nittany Valley, Pennsylvania, described by SHUSTER & WHITE, 1971) to form a well-documented data base.

5. The spread of characteristic groundwater values sampled in the Lambourn area boreholes requires explanation. A more extensive, possibly one-off, sampling network is required to check whether the isotopic pattern is related to any morphological, climatological or past recharge conditions. Ideally, the study would include other determinations (eg. of ^{14}C and of dissolved inert gases) to derive groundwater 'age' and provide other evidence of recharge characteristics.

6. An investigation specifically into the isotopic composition of evaporate from Malham Tarn is required to quantify more reliably the water mass balance. A suitable method would use pairs of evaporation pans, containing isotopically spiked water, which would be sampled at intervals, as suggested in a pilot study by ALLISON et al. (1979) in Ontario, Canada. This two pan method is preferred because of the changeability of meteorological conditions in the Malham area, which could not be easily accommodated in a single pan method. This field

study would provide an estimate of the limiting isotopic composition, δ^*, in equation (4.1) (section 4.3.2(a)). A further improvement could be made by direct sampling of atmospheric water vapour for isotopic analysis (δ_a), for example, by the pumped intake of air into a freezing unit, as performed by CRAIG & HORIBE (1967).

Practical applications

7. The identification of $\delta^{18}O$ variations up to 15 $^{o}/_{oo}$ in weekly precipitation in the U.K. recommends application of the natural tracing technique in systems in which response to rainfall is fast, with minimal opportunity for mixing and storage at this chosen timescale. Urban hydrology is suggested as a field of study which may benefit directly from examinations of isotopic variations. High impermeability of surfaces and low capacity for the retention of water maximise the probability of input signal identification in output waters.

8. Monitoring of stable isotopes to detect leakage from reservoirs is proposed as a practical application arising from the identification of the strongly seasonal signal in Malham Tarn. If further experimental work could be carried out to determine more accurately the parameters required for the exact estimation of evaporation amounts (recommendation 6), then mass balance calculations could be made. Areal and depth sampling of the reservoir and consideration of reservoir dynamics would be necessary, since a larger water body is less likely than the Tarn to fulfil the assumption of being well mixed.

5.3 The future of stable isotopes in the U.K.: concluding remarks

The stable isotope technique has been shown, by monthly and more intensive sampling over two full seasonal cycles, to have potential

value in future investigations in U.K. waters. The stable isotope input signal in precipitation over the U.K. has been found to be definable well beyond measurement error, although not strongly seasonal. The anticipated but important observation of isotopic invariance in predominantly diffuse-flow chalk waters has been confirmed by continued monitoring over the full period of sampling. It has been shown that, in specific conditions of fast throughput, an attenuated signal may be detected in output waters, and this provides considerable hydrological information. New evidence concerning mixing and storage of waters in the karst aquifer has been found and indicates the importance of water retention in the soil and upper aquifer. Novel information is provided by the stable isotopes in the identification of an evaporatively enhanced seasonal signal in Malham Tarn.

In general, interpretation of the stable isotope data, as exemplified by this study, is relient upon adequate monitoring of the input signal, upon the sampling of waters over considerable input variations and also upon the complementary information provided by conventional hydrological data. The natural tracing technique using stable isotopes may be considered as offering a new dimension in U.K. hydrology. The careful choice of situations where only partial mixing of the input waters or especially where signal enhancement occurs, can ensure a worthwhile contribution of the technique in future studies.

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APPENDICES

Appendix A: Isotope ratio measurement

Mass spectrometric measurement of the stable isotopes

The mass spectrometer used at AERE Harwell for the measurement of stable isotopes was of the Nier-McKinney style, the development of which was discussed in section 2.2.2. The model was a VG Isogas 602E. Figure 6.1 shows schematically the ion optics, which are central to the stable isotope measurement. The operating principles of the mass spectrometer are described in brief below:-

1. The gas to be analysed is admitted to the mass spectrometer under controlled conditions of high vacuum. Gas molecules are bombarded with electrons in the ion source, producing ions. The ions are drawn into a curved flight tube in which they are passed between the poles of a magnet and are deflected according to their mass.

2. The separated ion beams are focussed into two Faraday buckets in the 602E (a 'double collecting' mass spectrometer). These collect the charge carried by each ion and complex electronics produce a true ratio measurement of the ion currents.

3. A dual inlet system to the mass spectrometer admits alternately the sample gas and a reference gas. A McKinney changeover valve performs this automatically, without disturbing the ionisation conditions (McKINNEY et al. 1950). In the model used, 6 isotope ratios of each of the sample(S) and reference (R) gases are performed and the mean of the relative ratio difference calculated:-

$$\delta_{S-R} = \frac{R_{sample} - R_{reference}}{R_{reference}} \cdot 10^3 \quad (^{o}/_{oo}) \quad (6.1)$$

where R is the measured ion beam ratio (major mass beam to minor mass beam). The standard deviation of the ratios provides a check on the reliability of the measurement, and a continuous graph plot of ion beam strengths allows the operator to identify occasional problems, such as the inlet of impure gases into the analyser or drifting of the machine electronics.

Methods for the calculation of δ values for the stable isotopes are presented briefly below. For more full details of their derivations, the reader is referred elsewhere (CRAIG, 1957; GONFIANTINI, 1981), and for details with reference to operations in the Isotope Measurements Laboratory at AERE Harwell, to THORPE (1981).

Calculation of $\delta^{18}O_{SMOW}$

Dry CO_2 gas prepared by equilibration over the original water sample (section 3.4.1) is measured in the mass spectrometer against the Laboratory reference gas. This reference gas was produced by acidification of Carrera Marble; it is of known isotopic composition, and will be referred to as CM.

The desired ratio measurement for $\delta^{18}O$ calculation (CRAIG, 1957) is of

$$R_{18} = \frac{^{12}C^{16}O^{18}O}{^{12}C\ ^{16}O_2}$$

The actual ratio measured by the mass spectrometer is

$$R_{46} = \frac{\text{number of mass 46 ions collected}}{\text{number of mass 45 + mass 44 ions collected}}$$

giving the ratio difference δ^{46}_{S-CM}. Three stages of corrections are applied to the measured values:-

1. Correction for the amount and measured isotopic composition of cylinder CO_2 introduced in equilibration.
2. Correction for isotopic fractionation between CO_2 gas and water, assuming a fractionating factor, $\alpha_{(CO_2-H_2O)}$ of 1.0412 at 25°C for $^{18}O/^{16}O$ (FRIEDMAN & O'NEIL, 1977).

3. Correction to the water standard SMOW via the internal water standard H (bottled in one batch from the local East Hendred borehole). This has a measured $\delta^{18}O_{SMOW}$ value of -7.90 ± 0.11 °/oo.

The sum of the above corrections gives the following pair of calcuations for 5 ml water sample(s):-

$$\delta^{18}O_{S-SMOW} = 1.019\ \delta^{46}_{S-CM} - X$$

where $X = 1.019\ \delta^{46}_{H-CM} + 7.9$, and provides adjustment to ensure calibration between batches of samples. Routine precision of measurement is ± 0.1 °/oo (at 1σ).

Calculation of δD_{SMOW}

Direct measurements of SMOW samples, reduced to hydrogen gas, were included in batches of samples. The reference gas used for mass spectrometry was termed 103G. The actual mass beam ratio measured in the mass spectrometer was of mass 3 to mass 2; the relative difference for a sample is written δ^{3}_{S-103G}. Correction for tritium produced within the ion source was automatic in the operation of the VG Isogas 602E. The manipulation of equation (6.1) in δ-notation (section 2.2.4(b)) gives the final correction of

$$\delta D_{SMOW} = \frac{\delta^{3}_{S-103G} - \delta^{3}_{SMOW-103G}}{1 + \left[\delta^{3}_{SMOW-103G}\right] 10^{3}}$$

Routine precision of measurement is ± 1 °/oo (at 1σ).

Calculation of $\delta^{13}C_{PDB}$

Stable isotopes of carbon are expressed with respect to the PDB standard of limestone from the Pedee Belemnite formation. Mass spectrometric

measurement of the CO_2 evolved on sample acidification is made of both δ^{45} (mass 45/mass 44) and δ^{46} (as defined for $^{18}O/^{16}O$ measurement). Correction procedures are given by CRAIG (1957). Calibrations to the currently unavailable PDB standard, using intermediate standards, were performed by D.G. Humphries and R.L. Otlet of the Isotope Measurements Laboratory in April 1983, against the reference gas of CO_2 from Carrara Marble (CM). The following total correction is applied to mass spectrometric measurements:-

$$\delta^{13}C_{S-PDB} = 1.0695\ \delta^{45}_{S-CM} - 0.0338\ \delta^{46}_{S-CM} + 2.274$$

Routine precision of measurement is $\pm$ 0.3 $^{o}/oo$ (at 1σ).

Appendix B: Statistical procedures

a) Correlation

The Pearson product-moment correlation coefficient, r, between variables x and y is computed in this study:-

$$r = \frac{cov_{(x,y)}}{s_x s_y}$$

where $cov_{(x,y)}$ is the covariance of x and y, and s_x, s_y are the respective standard deviations of the variables. Tests of the null hypothesis that no correlation was observed between the variables (ie. H_o: r=0) were two-tailed t-tests. The following symbols are used in tables throughout the study to express the threshold levels of confidence at which the null hypothesis is being rejected in a two-tailed t-test of a particular parameter, for a sample population and (n-k) degrees of freedom:-

***	99% level of confidence
**	95% level of confidence
*	90% level of confidence
+	75% level of confidence
-	75% level of confidence

In the case of testing the r value, for example, *** indicates that a linear relationship is significant at the 99% level of confidence.

b) Simple regression

Linear least squares regression of the form:-

$$y = ax + b$$

is performed in the study, using the standard methods (eg. as described by

FERGUSON, 1974). Standard error (s_a) of the estimated slope parameter is given by:-

$$s_a = \frac{s_e}{s_x}\sqrt{\frac{1}{n}}$$

where $s_e = \sqrt{\frac{n}{n-2}\ [s_y^2\ (1-r^2)]}$

and n is the number of sample pairs in the regression. To calculate the standard error of the estimated intercept, a relatively special case, the method presented by DRAPER & SMITH (1966) is used. Significance testing of regression coefficients used the same procedure, and the same, symbolic representation in tables, as that described for correlation.

c) Multiple regression

Multiple regression, using the computerised Statistical Analysis System (SAS), calculates partial regression coefficients β_0, β_1, β_2 etc. for the corresponding variables X_0, X_1, X_2 etc. The procedure is identical to that discussed in terms of matrix algebra by DRAPER & SMITH(1966), and is presented by SAS INSTITUTE INC. (1982). Forward stepwise multiple regression is also performed by SAS. The forward selection technique begins with no variables in the model. Variables are added in turn, according to their contribution to explained variance in the dependent variable, as measured by the F statistic (describing the relative improvement in explanation brought about by the extra variable). Once a variable is in the model, it stays. Coefficients in the model are computed as for normal multiple regression, but by this procedure, total explained variance in the model is not necessarily maximised.