

BRITISH GEOLOGICAL SURVEY  
Natural Environment Research Council

**Fluid Processes Series**

**Technical Report WE/95/2**

The geochemical estimation of solute residence times  
in some reference hydrogeological settings

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December 1995

## PREFACE

The British Geological Survey has undertaken a project entitled: 'Geochemical validation of solute residence times: review and comparison for various geological environments'. This work has been funded jointly by the Commission of the European Communities and U.K. Nirex Ltd. The objectives of the project are to: compile relevant geochemical data for various European hydrogeological environments; review the validity of these data under various hydrogeological and geochemical conditions; assess the concept of 'reference' hydrogeological environments (RHEs) to illustrate principles, features and limitations of groundwater residence time estimations; and identify specific data needs and uncertainties.

The present report aims to provide a summary and synthesis of the project findings from the previous review phases by presenting tables and diagrams which illustrate the application of various solute and groundwater residence time indicators (solutes and oxygen and hydrogen isotopes) to a number of RHEs. This report gives a systematic approach and schematic guidance for estimating solute resident times in the reservoirs of different hydrogeological environments expected at a number of different deep radioactive waste repository scenarios. It constitutes the Final Report of the project and completes a series of project reports:

Crawford, M.B., Darling, W.G., Hooker, P.J. and Metcalfe, R. 1993. Geochemical validation of solute residence times: a review of the scientific basis for dating groundwaters. British Geological Survey Technical Report WE/93/4.

Darling, W.G., Metcalfe, R., Crawford, M.B and Hooker, P.J. 1994. The estimation of solute and groundwater residence times in different lithologies: a review of applications of methods. British Geological Survey Technical Report WE/94/43.

Matray, J.M. 1994. Origin and residence time of fluids from the clastic Keuper aquifer in the Paris Basin. British Geological Survey Technical Report WE/94/40 (prepared by J.M. Matray of BRGM, under contract to the British Geological Survey).

Metcalfe, R., Sen, M.A., Darling, W.G. and Hooker, P.J. 1995. The origins of salinity and constraints on solute fluxes in porewaters in some lake sediments from the English Lake District. British Geological Survey Technical Report WE/95/3.

## EXECUTIVE SUMMARY

This report assesses the concept of 'solute residence time' and considers whether the definition of 'reference' hydrogeological environments (RHEs) can be used to aid the geochemical estimation of solute residence times in groundwaters.

In general, previous studies of techniques for estimating groundwater 'ages' have emphasised determinations of the times since groundwaters were recharged. However, there have been relatively few assessments of the time for which solutes have been resident in the aqueous phase within a particular 'rock reservoir' (defined as a volume of rock, including all the matrix and fracture porosity which occurs within it). Such assessments need to be made during investigations of potential deep sites for the geological disposal of radioactive wastes.

For groundwaters, *solute* residence times are normally defined for steady state conditions as follows (Stumm and Morgan, 1981):

$$\tau_E = \frac{[E]V}{[E]_{in}q}$$

where  $[E]$  and  $[E]_{in}$  are the total concentration of solute in the system and the inflow respectively,  $V$  is the total volume of the groundwater, and  $q$  is the rate of groundwater infiltration. The 'residence time' in this case is simply the time that is required for the quantity of a solute that is present in the system at any instant, to be replaced completely by a fresh quantity of that solute. However, operational difficulties arise when this definition is applied to solutes in groundwater systems. This is because compositional gradients commonly arise along a groundwater flow path (even when such a system is at steady state), and also because samples are typically taken from point sources. Therefore, the total quantity of a solute that is present in a reservoir of interest is difficult to assess and a range of residence times will be estimated from waters sampled in different places along a groundwater flow-path. A more appropriate definition of solute residence time is the *maximum estimated* time for which a solute has been present within a rock reservoir of interest (or alternatively, the minimum time that would be taken to flush *all* the solute of a given type from the reservoir of interest).

There are three main types of technique that can be used in solute residence time studies:

1. Techniques that, under ideal circumstances, may yield quantitative residence time estimations;

2. Techniques that, under ideal circumstances, may yield quantitative, but limiting (maximum or minimum) residence time estimates;
3. Techniques that, under ideal circumstances, may yield only relative residence time indications.

The actual type of residence time estimate that may be made using a particular technique will depend partly upon the hydrogeological setting of the rock reservoir of interest. A particular technique that may yield quantitative residence time estimates under some circumstances, may yield only limiting residence time estimates under others.

If non-steady state conditions prevail, then the estimation of residence times for solutes in any rock reservoir becomes much more difficult or even impossible. In general, techniques that are potentially quantitative under steady state conditions will give only limiting residence times under non-steady state conditions. Techniques that may yield limiting or relative residence times under steady state conditions will also tend to yield limiting or relative residence times under non-steady state conditions.

Any hydrogeological environment can be considered to contain a number of different groundwater reservoirs (e.g. rock matrix, faults, an aquifer, an aquiclude, etc.), and a given solute will have a different residence time within each reservoir. Additionally, the 'ages' that are obtained may be an integration of the residence times of the water and/or solutes within a series of reservoirs, if the boundaries of the reservoirs are poorly defined. A set of rules is proposed for evaluating what type of residence time indication (quantitative, limiting or relative) might be obtained from a particular technique in any rock reservoir of interest. These rules are then applied to different rock reservoirs within each of seven different reference geological environments. These environments were chosen in order to represent a spectrum of hydrogeological environments within which potential radioactive waste repositories might be constructed:

1. Crystalline Shield Type
2. Argillaceous Rock Beneath Low-lying Plain Type
3. Coastal, Basin Margin Type
4. Salt Dome Beneath Low-lying Plain Type
5. Basin and Range Type
6. Argillaceous Rock in Foreland Basin Type
7. Sedimentary Basin at a Destructive Plate Margin Type

For each environment a table is presented which indicates what type of information might be obtained from each of the major techniques for estimating solute residence times. The aim is to

present a tool which might be used to design strategies for evaluating residence times of solutes in groundwaters.

It is possible to use such reference environments in order to establish priorities for the application of techniques. However, it is necessary for these techniques to be applied in conjunction with groundwater head data and geochemical data for the origins of the waters and their salinities. Such data enable the boundary conditions of rock reservoirs to be defined, and the flow paths of groundwaters to be constrained. A knowledge of groundwater flow paths is essential in order to make a thorough assessment of the applicability of a technique for groundwater dating.

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## 1. INTRODUCTION

The interpretation of both groundwater movements and the chemical evolution of groundwater/rock systems requires that residence times are estimated for dissolved constituents. Historically, research into this subject area has focussed on establishing groundwater 'ages'. Usually these are intervals of time since the groundwaters were recharged. The main aims of such studies have been generally to support models for groundwater flow, and to constrain the sizes of groundwater resources. However, the evaluation of potential sites for underground waste disposal requires that residence times are estimated for solutes in groundwaters from different sub-environments in the geosphere. Specifically, it is necessary to evaluate the periods of time for which solutes are likely to be resident within the aqueous phase that occupies any given volume of rock. For example, it may be desirable to show that the residence time of a *radionuclide in the groundwater* within a fault system, is shorter than the residence time of the *groundwater in the fault system*. Such an approach is particularly important in the case of radioactive waste disposal, where it is generally hoped that the geosphere will be a major barrier to pollutant migration for very long periods of time (of the order of c.  $10^5$  years).

Most techniques for groundwater 'dating' in the broader sense are based upon measurements of solute concentrations (or ratios of concentrations), and a knowledge of the rates of processes which affect these concentrations (or ratios of concentrations). Additionally, limits can be placed upon groundwater 'ages' by using the isotopic composition of the water ( $^{18}\text{O}$ ,  $^{16}\text{O}$ ,  $^2\text{H}$ ,  $^1\text{H}$ ,  $^3\text{H}$ ). Except for those cases where isotopic data for water are used, each of these techniques effectively uses a knowledge of the residence time of some solute. However, to date there has been no detailed assessment of the applicability of these various techniques to the estimation of solute residence times in general, in different sub-environments or reservoirs within water/rock systems. The purpose of the present report is to fill this gap by:

1. assessing the concept of 'residence time';
2. applying this concept to a number of 'dating' techniques, in order to assess how the residence times of the solutes used in the techniques might be estimated, in various different hydrogeological environments;
3. evaluating how these 'dating' techniques can be used in estimating the residence times of solutes in general (i.e. including solutes which do not form the basis of any dating technique).

In doing this, there are two underlying aims:

1. to produce documentation which can be used as a tool when designing strategies for estimating solute residence times;
2. to assess the value of using 'reference' hydrogeological environments (RHEs) as an aid to the development of strategies for estimating solute residence times.

## 2. THE CONCEPT OF RESIDENCE TIME

### 2.1 The general concept

#### 2.1.1 The relationship between 'solute residence times' and 'groundwater dates'

The estimation of solute residence times is distinct from (although related to) groundwater dating. Groundwater dating attempts to estimate the time for which a volume of water has been resident within a given rock reservoir. Most commonly, groundwater dating involves estimating the time since the water was recharged to a particular formation. In contrast, in estimating solute residence times it is necessary to consider how long the solute has resided within a given reservoir of interest. The latter will depend upon the goals of the particular study. In the context of radioactive waste repositories, it is useful to assess how long a solute resides in the fractures or pore-space within a given volume of rock. When defined in this way, a solute's residence time depends upon both the residence time of the solute in the water, and upon the residence time of the water in the rock reservoir of interest (defined to include the fracture and matrix porosity within a given volume of rock; Figure 1). *From now on, unless stated otherwise, the present report considers solute residence time from the perspective of a rock reservoir.* Thus, the report considers the rates of hydrochemical processes as water moves across a *rock* volume of interest. For example, Figures 2 and 3 illustrate schematically, several possible variations in solute concentration with time as a packet of water moves through a rock reservoir of interest.

In defining the concept of 'residence time' it is necessary to consider three different scenarios:

1. The system of interest is at steady state (i.e. processes of flow and solute/rock interactions occur at constant rates) and is spatially invariant (e.g. solute concentrations are constant throughout the rock reservoir of interest; Figure 2(i));
2. The system of interest is at steady state, but spatially variant (e.g. solute concentrations vary from place to place in the rock reservoir of interest; Figure 2(ii));
3. The system of interest is not at steady state (e.g. the rates of change of geochemical processes vary with time within the rock reservoir of interest; Figure 3).

### 2.1.2 Steady state and spatially invariant systems

Most commonly, 'residence time' is defined where the system of interest is homogeneous and does not change its character with time (Figure 1(i); Raiswell et al. 1984). In this case, 'residence time' is defined generally for any component in any reservoir (not just groundwater systems), as the abundance of the component in the reservoir, divided by the rate of input or output of that component, to or from the reservoir. Thus, solute residence times in groundwaters can be defined as follows (Stumm and Morgan, 1981):

$$\tau_E = \frac{[E]V}{[E]_{in}q} \quad (1)$$

where  $[E]$  and  $[E]_{in}$  are the total concentration of solute in the system and the inflow respectively,  $V$  is the total volume of the groundwater, and  $q$  is the rate of infiltration of the groundwater.

This definition is most easily applied to the first steady state scenario (Figure 2(i)). For example, some radionuclide in the water may be at secular equilibrium with the neutron flux in the host rock. Assuming that the rock reservoir is compositionally homogeneous, the concentration of the radionuclide at any instant will be constant throughout the reservoir, although it is being added continuously to the water by nuclear reactions involving the neutron flux through the rock, and being removed continuously from the water by radioactive decay. In this case, the residence time of the radionuclide can be calculated by dividing the concentration of the nuclide by the quantity which decays per unit volume of water per unit time. Clearly, in such cases, the residence time of a solute in a groundwater may be considerably less than the 'age' (time since recharge) of the water itself, depending on the half-life of the radionuclide.

### 2.1.3 Steady state, but spatially variant systems

Often, it will be difficult in practice to apply equation (1) when calculating solute residence times, because the concentration of a solute is spatially variable across the reservoir of interest (Figure 2(ii)). In such cases it may be difficult to estimate the total concentration of the solute in the reservoir with accuracy. Therefore, it is appropriate to adopt an operational definition of 'residence time' which is slightly different to that given by Equation (1) above:

$$\tau_E = \frac{[E]_{Outflow} - [E]_{Inflow}}{\text{Rate of Addition or Removal In Reservoir}} \quad (2)$$

where  $[E]_{\text{Outflow}}$  and  $[E]_{\text{Inflow}}$  are the concentrations of the solute in the outflow and inflow respectively, and the rate of addition or removal is expressed as the mass or moles of the solute added or removed from the reservoir per unit time per unit volume of water.

According to both definitions, 'residence times' under steady state conditions are effectively the minimum times which would be required for all the *actual* solutes present in a reservoir at any instant to be removed from that reservoir. In other words, all the atoms/molecules of a given solute that are present in a reservoir at a time  $T_0$  would not be displaced by other atoms/molecules of the solute until at least a time  $T_0 + \tau_E$  (of course mixing processes within the reservoir might mean that a given atom or molecule of the solute might persist within the reservoir for a time longer than  $\tau_E$ ).

#### 2.1.4 Non-steady state systems

In the case of non-steady state conditions, there is a temporal variation in the overall character of the system of interest, and meaningful residence times will generally be much harder to estimate than under steady state conditions. In such cases, the rates of addition or removal of a solute, to or from the water, will vary with time (Figure 3). Only in circumstances where the time-dependence of these variable rates is known will it be possible for quantitative solute residence times to be determined e.g. if the solute is a radionuclide with a known half-life then some quantitative limits on residence time may be possible.

If the rates of change of processes that affect solute concentrations increase with time (solute A in Figure 3), then the residence times that are calculated from the *present* rates of these processes will underestimate solute residence times. Conversely, if the rates of such processes decrease with time (solute B in Figure 3), then the residence times that are calculated from the *present* rates of these processes will be overestimates.

In any rock reservoir it is possible that some solutes will have achieved steady state even if others have not achieved such a state. Therefore, in designing strategies for estimating residence times, it is appropriate to give a high priority to those techniques which rely on solutes that are most likely to have achieved a steady state in the reservoir of interest.

#### 2.1.5 The significance of boundary conditions

The groundwater conditions at the boundary of a rock reservoir may be an important control on whether or not the concentrations of dissolved solutes reach steady state within the reservoir. Clearly, if variable concentrations of a solute are introduced to a reservoir, then steady state conditions will not apply unless processes such as water/rock interaction within the reservoir are

rapid in comparison to the rates with which the input concentrations vary (in this case the system within the reservoir can be considered to be instantaneously at steady state). Therefore, a departure from steady state is more likely for those techniques for estimating residence times that are applicable to long time-scales, than for those techniques that are applicable to shorter time-scales.

## 2.2 Application of the concept to actual groundwater samples

A key feature of the concept of 'residence time' is that, whichever definition is applied, residence times must be specified with reference to some reservoir. In the case of aqueous solutes, it is essential to specify the volume of water or the volume of rock (including matrix and fracture porosity), in which the solutes are resident.

An important problem which is often encountered, is that the residence time of a solute in a reservoir must be evaluated using groundwater samples from a limited number of point sources. From these it is necessary to estimate the residence times of solutes in reservoirs with volumes that are normally many orders of magnitude larger than the volume of a given sample. When the residence time of a solute is estimated for different samples from the same reservoir, then different 'ages' will normally be calculated (Figure 4). Conceptually, this can be related to the steady-state definitions of residence time given in Section 2.1, by considering each sample to lie on one boundary of a different sub-reservoir within the reservoir of interest. For example, Figure 4 illustrates an aquifer from which three water samples are taken, each with a different concentration of  $^{14}\text{C}$ . Each sample can be thought of as lying at the down-flow boundary of a different sub-reservoir within the larger reservoir represented by the aquifer. The age which is calculated from the  $^{14}\text{C}$  content of each water sample is the time since the water was recharged. Thus, each age represents the maximum time for which water has been present within the sub-reservoir that is bounded by the upper and lower margins of the aquifer, by the sampling point on the down-flow side, and by the recharge point on the up-flow side. This definition of residence time is implicit in Equation 2. It follows that the maximum time for which a given volume of water has been resident within the reservoir equals the minimum time needed to flush *all* the solute from the reservoir completely.

Many groundwaters are in fact mixtures of different waters which may have had very different histories. If the characteristics and proportions of the components of the mixtures can be identified, then it may be possible to calculate residence times. In circumstances where mixing has occurred, the techniques for estimating solute residence times are used in similar ways to those when there is only a single source to the groundwater. The underlying principle is to calculate a mean input of solute to the rock reservoir of interest before applying the technique for estimating solute residence times (Figure 5).

### 2.3 Application of geochemical data to the evaluation of solute residence times

There are three principal applications of geochemical data to the estimation of solute residence times:

1. in the identification of rock reservoirs which have contained a given water in the past;
2. in the identification of different components to the water within any rock reservoir of interest;
3. in the estimation of residence times, using a knowledge of the rates of geochemical processes which affect the concentrations of solutes (or the isotopic composition of the *water* in the special cases of  $^3\text{H}$ ,  $^2\text{H}$ ,  $^1\text{H}$ ,  $^{16}\text{O}$  and  $^{18}\text{O}$ ).

Each of these applications is an essential aspect of any study of solute residence times. The first application is important because the applicability of any groundwater 'dating' technique in estimating the residence times of solutes will depend partly upon which rock reservoirs have been entered by the water. For example, if a water in a sandstone aquifer contains no detectable  $^{14}\text{C}$ , two possible explanations can be invoked:

1. that the water originally contained  $^{14}\text{C}$ , at levels consistent with atmospheric recharge, but this has since decayed (hence the residence times of many of the other solutes in groundwaters within the sandstone aquifer may be  $> c. 30 \text{ ka}$ ).
2. that any  $^{14}\text{C}$  in the water had decayed substantially *before* the water entered the sandstone aquifer (hence, no constraints can be placed upon the residence times of solutes in groundwaters within the sandstone aquifer, unless the hydrodynamic system today is the same as in the past, and the level of  $^{14}\text{C}$  in the input waters to the reservoir can be measured).

Geochemical data may help to distinguish between these possibilities by helping to constrain the boundary conditions of the reservoir and providing evidence that the water has (or has not) resided solely within the sandstone reservoir.

Geochemical data can be invaluable for identifying where mixing actually occurs, and for enabling the effects of such mixing to be calculated. Such data may also provide important evidence for the relative proportions of the various water components. This might then be used to calculate the rates of solute input into the reservoir of interest.

Geochemical data can be used to estimate residence times in three different senses:

1. Quantitative apparent residence times can be estimated where numerical values can be placed on the rates of the processes that affect the concentrations of a particular residence time indicator. All the inputs of the residence time indicator to a reservoir must be known, and it must be possible to allow for effects such as mixing between different waters and water/rock interactions. Radiocarbon 'dating' of waters is an example of this type of residence time estimate.
2. Quantitative limits can be placed on the residence times of solutes in certain cases where the rates of the processes that affect the concentrations of a particular residence time indicator are unknown. The residence time limit is deduced from the presence or absence of a particular residence time indicator, the attainment of equilibrium between a solute and the rock, or the occurrence of disequilibrium between a solute and the rock. For example, if a peak in levels of  $^{36}\text{Cl}$  in waters from a shallow groundwater aquifer are above the levels for present-day recharge and secular equilibrium, then the residence time of the water in the reservoir is likely to have been less than c. 30 years (the peak in concentrations being attributable to nuclear bomb detonations). Such a conclusion is independent of whether or not phenomena such as mixing between different waters and water/rock interactions have occurred.
3. Relative residence time estimates can be made in certain cases where the rates of relevant geochemical processes are unknown, and the presence or absence of solutes or equilibrium conditions are not diagnostic of limiting residence times. The *direction* of some geochemical process over time must be known in order to estimate relative residence times. An example of such a process is the progressive dissolution of aquifer minerals as a water migrates through an aquifer. This results in the water becoming a more concentrated solution, although the rate at which it does so is unknown. In such cases, it can be inferred that more concentrated waters are likely to have resided within the rock for a longer time than more dilute waters. Relative residence time estimates may be possible in two distinct senses:
  - a. different solutes in a given reservoir may be placed in order according to their residence times within the reservoir of interest;
  - b. the residence time of a given solute in one reservoir may be specified relative to the residence time of the same solute in a different reservoir.

Certain indicators of residence time are capable of allowing only relative times to be estimated while other indicators of residence time may allow only limiting or relative times to be estimated. Residence time indicators which may under ideal circumstances allow quantitative residence time estimates to be made may, in other situations, allow only limiting or relative residence times to be inferred. In other words, the exact type of residence time estimate that might be obtained from any given data will depend not only upon the nature of the residence time indicator, but also upon the particular rock reservoir which is being considered.

### **3. REFERENCE HYDROGEOLOGICAL ENVIRONMENTS (RHEs)**

#### **3.1 The concept of Reference Hydrogeological Environments (RHEs)**

It is desirable to specify RHEs in order to provide a framework for the rapid development of strategies to be used in actual hydrogeological investigations. Ideally, basic elements of a strategy for investigation should be specified for each reference environment. Any site investigation could then build upon those elements of strategy corresponding to the RHE that most closely matches the actual site of interest.

However, it is difficult to apply this concept of RHEs to the estimation of solute residence times. This is because practically every hydrogeological setting is unique, and many factors can affect the choice of techniques that are used to estimate residence times. Therefore, it would not be useful to specify detailed reference environments with corresponding detailed strategies for estimating solute residence times. Nevertheless, a given technique for estimating solute residence times will be more applicable to some types of groundwater reservoir than to others. For example,  $^{14}\text{C}$  is more likely to be a useful residence time indicator in a shallow groundwater aquifer at depths of a few hundred metres, than in basement rock at depths of several kilometres. Similarly, a given type of groundwater reservoir will be more important in some hydrogeological settings than in others. For example, faults might be relatively more important reservoirs in crystalline basement from an active tectonic belt than in sedimentary basins from a tectonically inactive continental interior. For these reasons the present report gives an indication of the *likely* applicability of each technique, to each major water reservoir within several different hydrogeological environments. The aim is to present a tool to help set priorities for data acquisition in any given hydrogeological environment.

#### **3.2 Choice of RHEs**

The specification of RHEs has been guided by the various settings which have been proposed as possible hosts for radioactive waste repositories. Each environment is *not* intended to be a representation of any actual environment that is being investigated for its suitability to host a



repository. However, each reference environment has been devised so as to incorporate specific features which do occur in the environs of potential radioactive waste repositories.

The range of RHEs has been chosen to span the range of tectonic activity that is shown by the settings of possible radioactive waste repositories around the world. These reference environments are illustrated schematically in Figures 9 to 15, which are arranged approximately in order of increasing tectonic activity, as follows:

1. The Crystalline Shield Type RHE.
2. The Argillaceous Rock Beneath Low-lying Plain Type RHE.
3. The Coastal, Basin Margin Type RHE.
4. The Salt Dome Beneath Low-lying Plain Type RHE.
5. The Basin and Range Type RHE.
6. The Argillaceous Rock in Foreland Basin Type RHE.
7. The Sedimentary Basin at a Destructive Plate Margin Type RHE.

### **3.3 Rules for assessing the applicability of techniques**

#### **3.3.1 A scheme for classifying techniques**

As stated previously, a major aim of this report is to present a tool which might be used to aid the development of strategies for estimating solute residence times in groundwaters. However, it is not possible to specify a 'best' technique by which solute residence times can be evaluated in any given setting, because this will depend upon:

1. The specific aims of the particular study;
2. Specific operational factors, such as the natures of the sampling equipment and the analytical facilities which are available;
3. The particular characteristics of the hydrogeological setting of interest.

A particular study might require only an upper or lower limit to be placed upon solute residence times. Therefore, it might be appropriate for that study to give a higher priority to techniques which can only indicate limiting residence times, than to more elaborate (and possibly more expensive) techniques that might yield quantitative apparent ages. However, a different study might require quantitative, apparent residence times to be estimated, and hence the opposite priorities might be set for data acquisition. Therefore, it is inappropriate to indicate a 'degree of usefulness' for each technique. Instead, the approach which has been adopted here has been to indicate the *type* of information which can be obtained by applying any given technique in any reservoir of interest. Each technique has been classified according to its applicability as follows:

- Q The technique can give **quantitative** residence times;
- L The technique can give numerical **limits** to residence times;
- R The technique can give an indication of **relative** residence times;
- O The technique is probably inapplicable.

When assigning these designations to the various techniques for estimating solute residence times, each technique is considered in isolation. It is possible that there may be indirect methods of estimating the residence time of a particular solute (for example, by using data for  $^{14}\text{C}$  to estimate a residence time for Na), but these are not considered here.

Clearly, the classification of any technique is somewhat subjective, since the definitions of 'quantitative', 'limiting' and 'relative' residence times are dependent upon the problem being investigated. For example, noble gas solubility data may yield recharge temperatures that can be used to estimate the time of recharge, if the past variation in climatic conditions is known from independent evidence such as pollen data. However, groundwater mixing processes normally lead to the temperatures calculated from noble gases being averages of the actual recharge temperatures over a number of years. Therefore, it may be possible to show only that the temperature of recharge was similar to modern recharge temperatures averaged over several decades. In the present report, an account is taken of the likely time required for a water to cross the reservoir of interest when classifying a technique according to its applicability for estimating residence times. Therefore, in the case of a reservoir in the unsaturated zone, across which water will move in a relatively short time, noble gas data are likely to indicate temperatures similar to the present. In this case, they will yield limiting residence times. In contrast, in an aquifer beneath the water table, across which water might take many thousands of years to move, noble gas data might indicate a range of residence times. In this case, the noble gases would be considered to yield quantitative residence times.

### 3.3.2 Assessment of the 'ideal' applicability of a technique

Since each hydrogeological setting will be unique, the designation (Q, L, R or O) which is given to any technique will not be applicable universally, to all types of reservoir in all types of setting. Therefore, a designation has been applied to each technique by considering the type of information that can be obtained from the technique, *under ideal circumstances*, given the current state of knowledge about the behaviour of solutes in groundwater systems (e.g. where  $^{14}\text{C}$  is detected in a groundwater, and allowance can be made for groundwater mixing, water/rock interaction, contamination during sampling etc, then a quantitative residence time estimate might be possible). In making this assessment, it is assumed that the residence time indicator occurs in an ideal groundwater system in which:

1. all the relevant fluxes into a reservoir can be quantified;
2. relevant data can be acquired from anywhere in the reservoir;
3. the hydrological flow system is at steady state and has always been at steady state (that is, the system is the same today as it has always been).

When these rules are applied, a given technique for estimating solute residence times might be given different applicability designations in different reservoirs. For example,  $^{14}\text{C}$  data could, under favourable circumstances, yield quantitative residence time estimates for this radionuclide. Therefore, if it is concluded that  $^{14}\text{C}$  probably occurs in the reservoir of interest, and that groundwater mixing is unlikely, then a designation of 'Q' would be appropriate. However, if it is considered that  $^{14}\text{C}$  is probably absent from the water input to a rock reservoir of interest, then  $^{14}\text{C}$  would be of no use for residence time indications *in that reservoir* and the applicability of this technique would be designated as 'O'. An exception to this is the special case where a confined aquifer is considered to be the reservoir of interest. In this instance, an absence of  $^{14}\text{C}$  would indicate that the water had been isolated from the recharge area for more than c. 30 ka, and it would be appropriate to designate the applicability of  $^{14}\text{C}$  to residence time studies by 'L'.

This approach aims to minimise ambiguities in the designations, where there is some uncertainty about the type of residence time information which might be gained from a particular technique. Such uncertainties are particularly likely to arise in the cases of techniques that are relatively new, such as those that employ  $^{36}\text{Cl}$  and  $^{129}\text{I}$  data. In these cases, there has been some debate in the literature about whether fully quantitative residence time estimates can ever be made, owing to the subsurface generation of  $^{36}\text{Cl}$  and  $^{129}\text{I}$ . However, theoretically, under ideal circumstances, these

isotopes could be used to derive quantitative residence time estimates, and there have been some published attempts to do this. Thus, these basic techniques are assigned 'best case' designations of 'Q'. Conversely, it could be argued that the gross chemical evolution of a water along a flow path could yield quantitative residence time information, provided that the rates of all relevant water/rock interactions are known. However, clearly, such information is beyond the current understanding of groundwater systems, and hence the gross chemical evolution of a water can be used only to give qualitative, relative residence time information.

The 'ideal' applicability of each major technique for estimating solute residence times is given in Table 1.

### 3.3.3 Assessment of the likely applicability of a technique in the actual groundwater reservoir of interest

Having classified each technique according to its ideal applicability it is necessary to classify it according to its applicability in a given situation of interest. This can be done by considering:

1. the *most probable* behaviour of the residence time indicators in the reservoir of interest (e.g. whether or not  $^{14}\text{C}$  is likely to be present in the reservoir of interest);
2. the *most probable* magnitudes of all solute fluxes into the reservoir of interest (e.g. whether or not the  $^{14}\text{C}$  originates solely from one source of water).

In order to minimise ambiguities in assigning a designation to each technique for estimating solute residence times, a scheme has been devised that is based on answers to the following questions:

1. What is the applicability of the technique under ideal conditions ?
2. Can variations in solute concentrations or ratios of isotopes/solutes be expected across the reservoir of interest ?
3. Is the continuous variation in past inputs of solutes to the reservoir known ?
4. Is the system at steady state ?
5. Can the residence time indicator be measured anywhere in the reservoir (i.e. is the indicator present throughout the reservoir or is it absent in some places) ?

6. Are the mean values (of concentrations, or ratios of solutes or isotopes) in the reservoir different to the mean values in the inputs to the reservoir ?
7. Do the mean values (of concentrations, or ratios of solutes or isotopes) show a continuous variation across the reservoir of interest ?
8. If the reservoir were to be isolated, would the mean values (of concentrations, or ratios of solutes or isotopes) remain constant over time ?

The applicabilities are chosen by answering these questions according to the scheme in Figure 6.

The application of this scheme of classification to a simple hydrogeological system is demonstrated in Figure 8. This illustrates a granite that is overlain by a succession of shale and sandstone, and which is cut by a normal fault. Six different groundwater/solute reservoirs within this system are listed in Table 2, and different possible behaviours of three solutes (A, B, and C) are illustrated graphically on the cross-section. Each graph illustrates the *relative* changes in concentrations that are shown by the solutes as a 'packet' of water migrates across each reservoir. For example, as a given volume of water moves across the sandstone above the water table (Reservoir 1), the concentration of A remains constant, the concentration of B shows a slight increase, and the concentration of C shows a marked decrease. The solute A cannot be used as a quantitative indicator of residence time within this reservoir because it shows no time-dependent variation in the reservoir. If the solute A is  $^{14}\text{C}$  (in which case the constant concentration might be due to the water moving across the water table relatively rapidly in comparison to the rate of radioactive decay) then it is likely that it will have a high concentration relative to deeper groundwaters. Under ideal conditions it would be possible to use the  $^{14}\text{C}$  data to place limits on the residence time of  $^{14}\text{C}$  within the Reservoir 1, and it could be given a designation of 'L'.

### **3.4 The applicability of techniques for estimating solute residence times in the RHEs**

Tables 3 to 9 indicate the applicability of each of a number of techniques to estimating solute residence times in several groundwater reservoirs within each RHE (Figures 9 to 15). The techniques are arranged so that in each Table, those capable of yielding quantitative estimates appear at the left, while those that are capable of giving only relative residence times are located towards the right. Additionally, techniques that rely on radioactive isotopes with short half-lives are placed further to the left than those that rely on radioactive isotopes with longer half-lives.

From Tables 3 to 9 and Figures 9 to 15, it is apparent that a major factor in controlling the applicability of each technique is the overall nature of the groundwater flow system in each

reference hydrogeological setting. It is this that controls the inputs to, and outputs from, any given rock reservoir. For example, if a groundwater flows across a fault,  $^{14}\text{C}$  may be of little use in constraining the residence time of the water in the fault zone (Figure 11; Table 5), but if water flows along a fault then  $^{14}\text{C}$  may enable limiting residence time estimates (Figure 13; Table 7). Clearly, the geometry of the groundwater flow system is partly controlled by the tectonic setting of the environment. However, the climatic conditions in any given setting are also an important control on groundwater flow. Therefore, when using the Tables to develop a strategy for estimating solute residence times, it is necessary to consider both the physical characteristics *and* climate of both the environment of interest and a reference environment.

Serious potential limitations to the use of RHEs in solute residence time studies arise because groundwater flow systems may vary over time, both in response to tectonic activity (at least near to zones of mountain building and/or subduction of oceanic crust) and climatic changes. This affects the application of solute residence time indicators in two main ways:

1. Non-steady state or transient conditions might prevail over long periods of time. This might cause the current hydrogeological system in an area of interest to reflect ancient hydrogeological conditions rather than modern conditions. For example, the magnitudes and directions of groundwater flow today might in fact reflect ancient periods of uplift or subsidence.
2. The groundwater that is currently present in a particular rock reservoir of interest may have had a history that is substantially different to that which might be expected from a consideration of the modern pattern of groundwater flow. This is important, because it is necessary to identify all the groundwater and solute inputs to a particular rock reservoir in order to make reliable residence time estimates.

In order to minimise these potential pitfalls it is highly desirable that the various techniques for assessing solute residence times are used in conjunction with:

1. all available geochemical evidence for the origins of a water and its salinity;
2. hydraulic data from which groundwater fluxes can be elicited.

### **3.5 The application of the RHEs in developing strategies for estimating solute residence times**

Figures 9 to 15 and Tables 3 to 9 can be used to set priorities for the acquisition of data to be used to estimate solute residence times in potential deep repository scenarios. When doing this, it is

important to avoid simply selecting a reference environment that is similar to the actual environment of interest, but to consider both the similarities and differences between *each* reference environment and the actual environment. In this way an environment that matches the actual potential repository environment can be constructed from several different RHEs.

Tables 3 to 9 indicate the type of residence time estimate that is possible from a given technique under *ideal* circumstances. Therefore, the Tables can be used to avoid adopting techniques that are incapable of giving the type of information that is required for a site characterisation study.

#### 4. CONCLUSIONS

Up to the present, most published studies of groundwater 'dating' have focussed on estimating the time that has elapsed since a groundwater was recharged. However, there have been relatively few assessments of the time for which solutes have been resident in the aqueous phase within a given volume of rock. Such assessments may be helpful in investigations of potential deep sites for the geological disposal of radioactive wastes.

The 'residence time' of some component in some reservoir is normally defined for systems at steady state in which the component of interest is added to and removed from the reservoir at the same rates. Thus the 'residence time' is simply the time that is required for the quantity of the component that is present in the reservoir at any instant, to be replaced completely by a fresh quantity of that component. This definition can be applied irrespective of whether the system is spatially variant or invariant. However, operational difficulties arise when this definition is applied to solutes in groundwater systems. This is because compositional gradients commonly arise along a groundwater flow path, and samples are typically taken from point sources. Therefore, the total quantity of a solute that is present in a reservoir of interest is difficult to assess. This problem can be circumvented by considering a sampling point to lie on the down-flow margin of a rock reservoir. A more appropriate definition of solute residence time is then the *maximum* time for which a particular solute has been present within that reservoir. This is equivalent to the *minimum* time that it would take to flush all the solute from the reservoir, given the conditions of steady state and the temporal invariance of all relevant processes e.g. groundwater flow and water/rock interactions. If non-steady state conditions prevail, then the estimation of residence times for solutes in any rock reservoir becomes much more difficult or even impossible. In general, techniques that are potentially quantitative under steady state conditions will give only limiting residence times under non-steady state conditions. Techniques that may yield limiting or relative residence times under steady state conditions will also tend to yield limiting or relative residence times under non-steady state conditions.

The concept of RHEs is useful in establishing a framework for the development of strategies for estimating solute residence times. In particular, it is possible to use such environments in order to establish priorities for the application of techniques. However, it is necessary for these techniques to be applied in conjunction with groundwater head data and geochemical data for the origins of the waters and their salinities. This is because there is a relationship between the geometry of any given groundwater flow system and the applicability of any given technique for estimating solute residence times:

## 5. REFERENCES

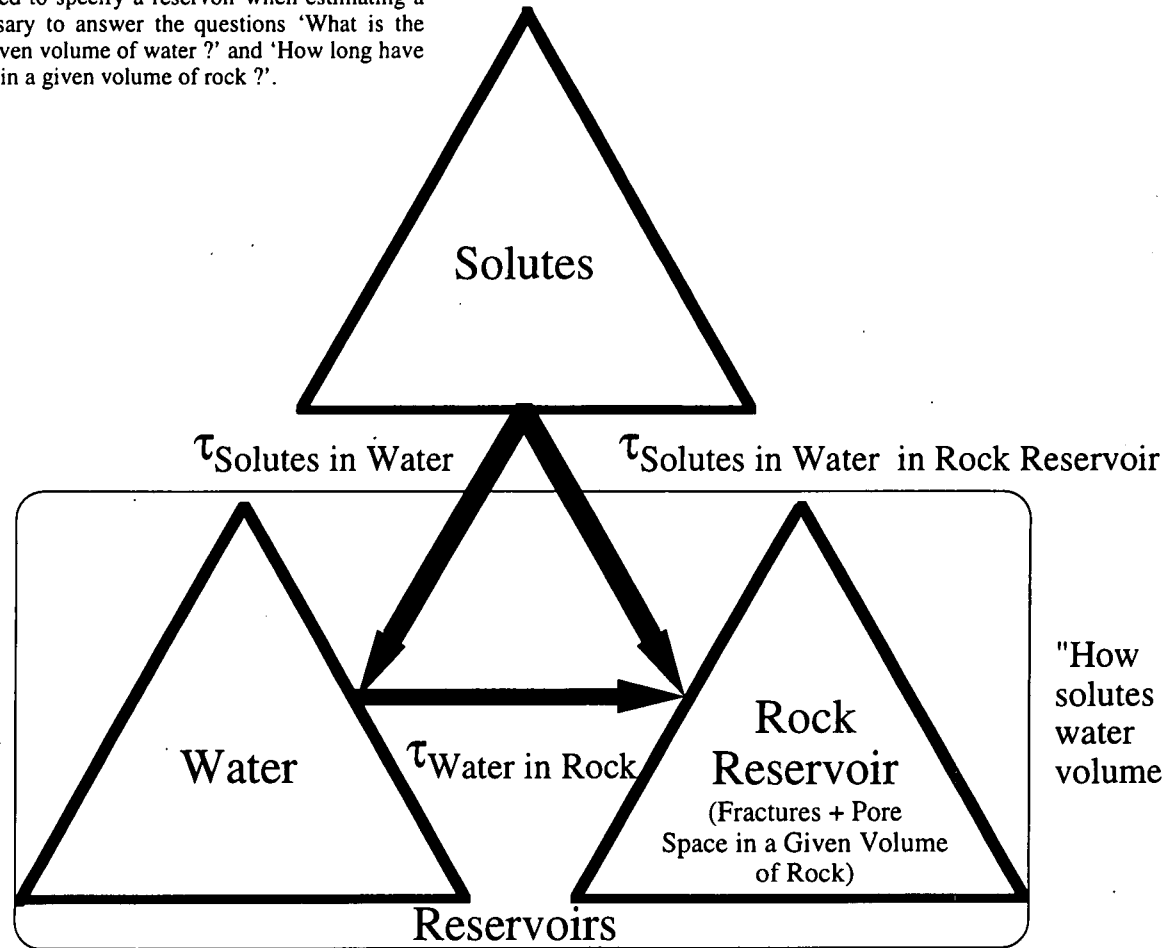
Raiswell, R.W, Brimblecome, P., Dent, D.L. and Liss, P.S. 1984. *Environmental Chemistry*. Edward Arnold, London. 184pp.

Stumm, W. and Morgan, J.J. 1981. *Aquatic Chemistry*. John Wiley & Sons.



**Figure 1**

Schematic diagram justifying the need to specify a reservoir when estimating a solute's residence time. It is necessary to answer the questions 'What is the residence time of a solute within a given volume of water?' and 'How long have the solutes been mobile in water within a given volume of rock?'.  
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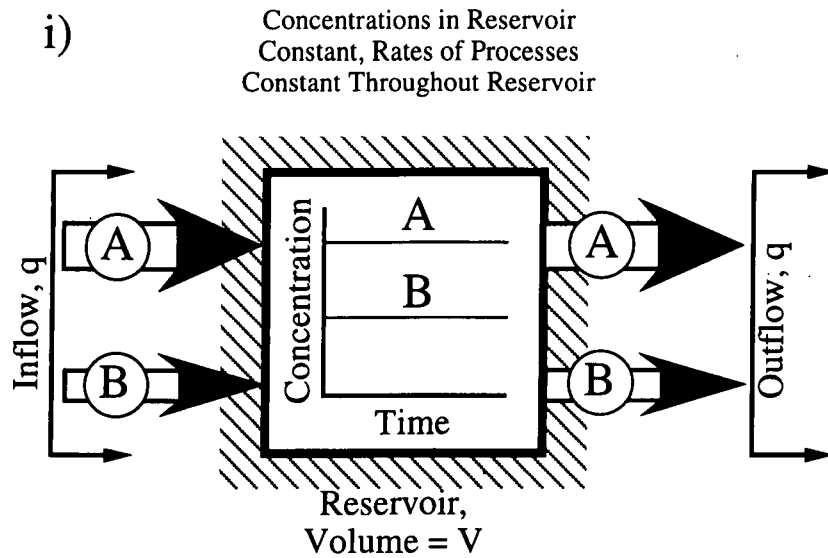
"What is the residence time of solutes in a given volume of water?"

"How long have the solutes been mobile in water within a given volume of rock?"

Figure 2

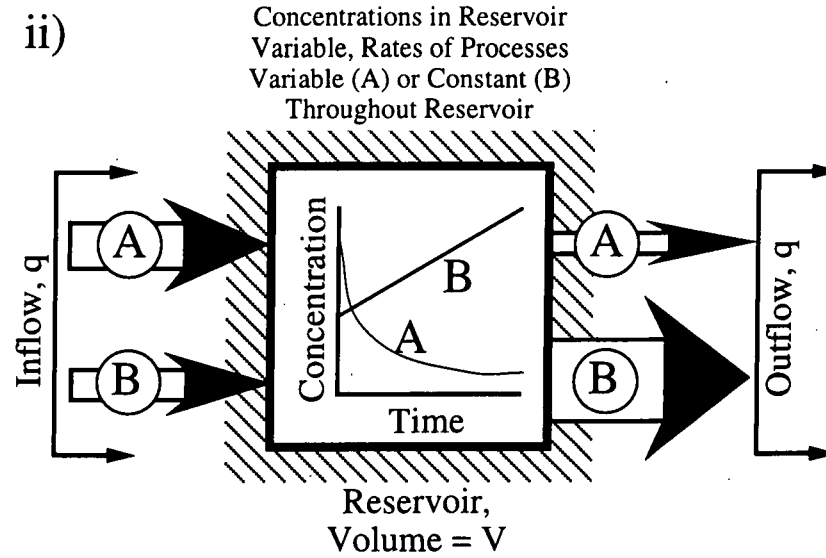
The estimation of solute residence times in groundwater systems at steady state. In both i) and ii), the graphs illustrate the variations in concentrations of solutes A and B within a given volume of water as the water moves through a rock reservoir. i). As water moves through a rock reservoir, the concentrations of the solutes A and B remain constant. The residence times of the solutes are defined according to Equation 1. ii). As water moves through a rock reservoir, the concentration of solute A decreases at a variable rate, and the concentration of solute B increases. The residence time of a solute is calculated from the rates of processes in the reservoir which affect the concentrations of the solutes, and of the initial and final concentrations of the solutes.

Both Steady State, Graphs Show Variations As a Volume of Water Moves Across The Reservoir



Solutes:  $\left[ \begin{matrix} \text{A} \\ \text{B} \end{matrix} \right]$  e.g. Solutes equilibrated with minerals in the reservoir

$$\tau_{A,B} = \frac{[A,B] \cdot V}{[A,B]_{in} \cdot q}$$

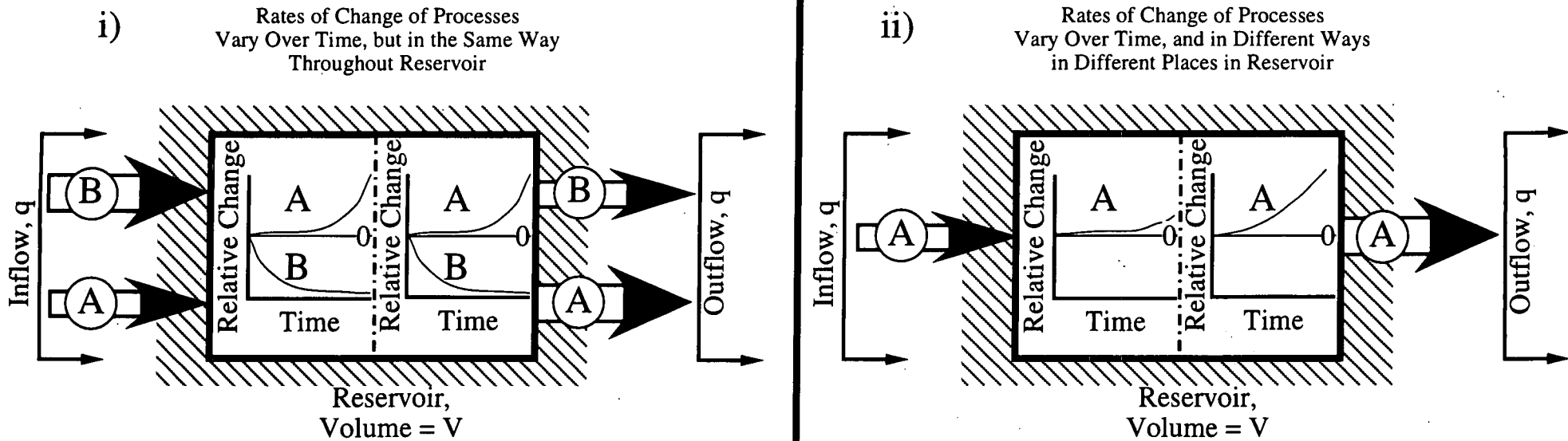


Solutes:  $\left[ \begin{matrix} \text{A} \\ \text{B} \end{matrix} \right]$  e.g.  $^{14}\text{C}$ , decays over time (steady state only if input concentration invariant)  
 e.g.  $^4\text{He}$ , contributed over time by aquifer

$$\tau_{A,B} = \frac{[A,B]_{Outflow} - [A,B]_{Inflow}}{\text{Rate Addition Or Removal In Reservoir}}$$

**Figure 3** The estimation of solute residence times in groundwater systems that are not at steady state. In both i) and ii), the graphs illustrate relative variations in solute concentrations (i.e increases or decreases compared to the starting value) with time at each of two given points in the rock reservoir. Residence times can be estimated only if the variations of the rates of change of concentrations over time are known.

**Both Non-Steady State: Graphs Show Variations At Two Different Points In Reservoir**



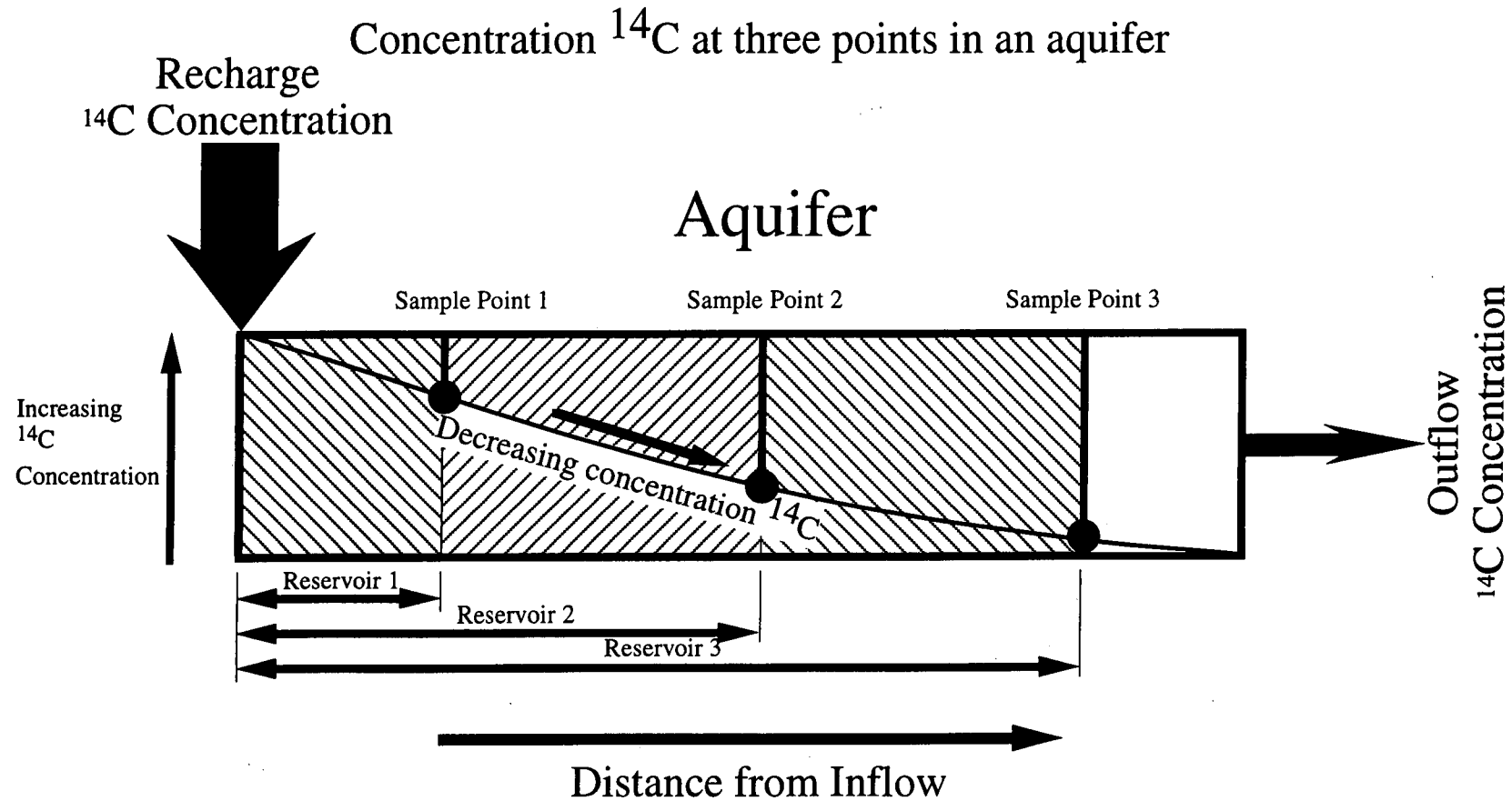
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- Solutes:**
- (A)** e.g. Solubility increases during uniform heating of reservoir
  - (B)** e.g. Solute decreases over time due to uniform cooling of reservoir over time

- Solutes:**
- (A)** e.g. Non-uniform heating leading to temperature gradient across reservoir

$\tau$  Estimated only if Rate of Change of Rates Known

**Figure 4** Schematic illustration of the variation in concentration of a solute ( $^{14}\text{C}$ ) along a flow path in an aquifer. The time which is calculated from the concentration of the solute at each sampling point is actually the time for which the solute has been resident within the aquifer on the up-flow side of the sampling point. The aquifer can be thought of as being divided into a number of sub-reservoirs. The residence times which are calculated for sampling points 1, 2 and 3 relate to reservoirs 1, 2, and 3 respectively.



$\tau_{^{14}\text{C}}$ , Reservoir 1 from  $[^{14}\text{C}]$  at sampling point 1

$\tau_{^{14}\text{C}}$ , Reservoir 2 from  $[^{14}\text{C}]$  at sampling point 2

$\tau_{^{14}\text{C}}$ , Reservoir 3 from  $[^{14}\text{C}]$  at sampling point 3

**Figure 5** Schematic illustration of the importance of allowing for groundwater and solute mixing when estimating solute residence times. The residence time is calculated using the same basic method as that illustrated in Figure 2(ii). However, the concentration of the solute A in the total inflow must be used in the calculation. This is the weighted mean of the contributions of different waters to the mixed water which occupies the rock reservoir of interest.

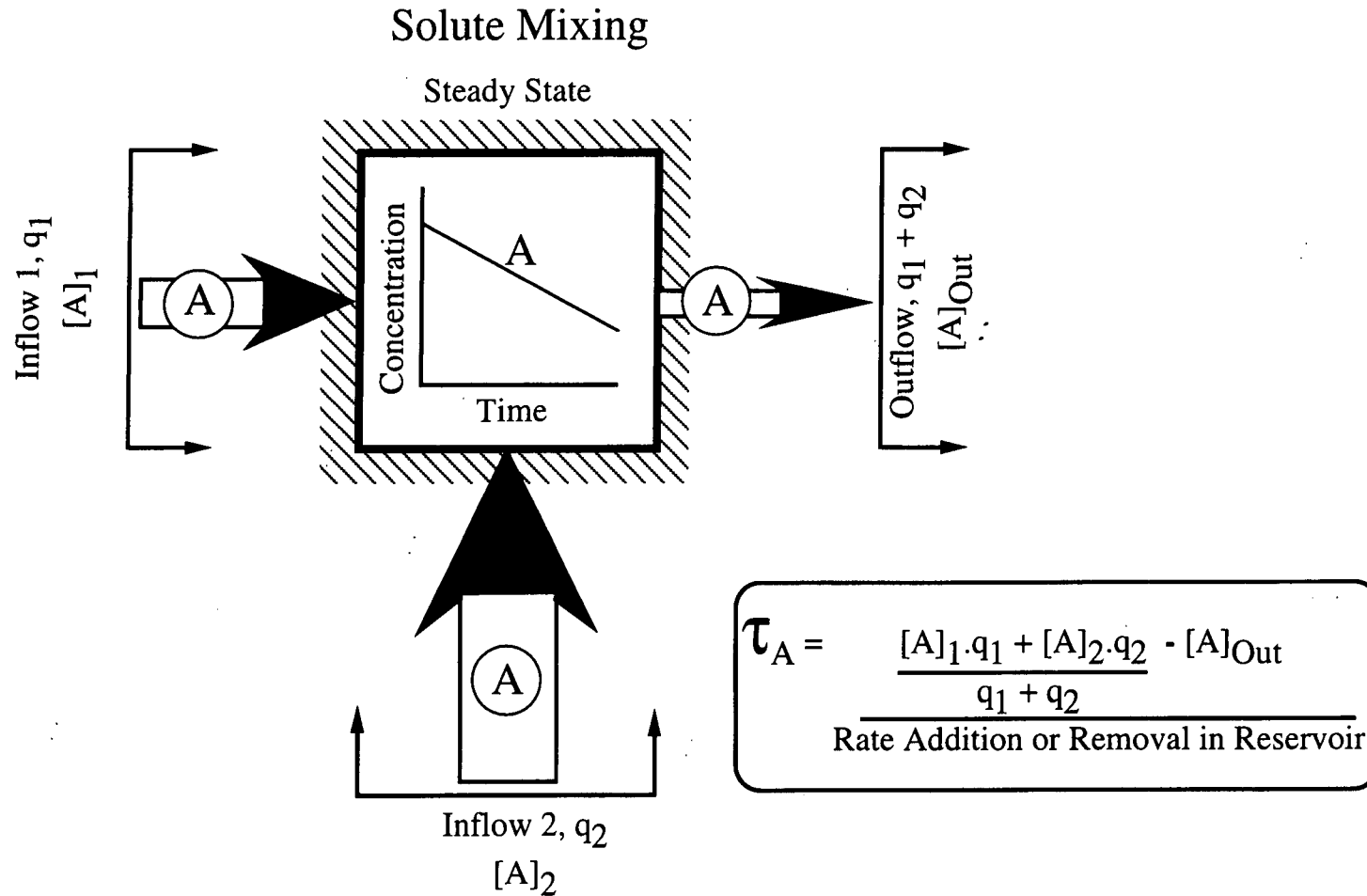


Table 1 'Ideal' applicability for each major technique for estimating solute residence times

Tracer on which technique based	Principle behind technique	'Ideal' Applicability
<sup>3</sup> H	Radioactive decay from known time of anthropogenic input	Q
CFC's	Known time of anthropogenic input and known variation in atmospheric concentration	Q
Agri-chemicals	Known time of anthropogenic input	L
<sup>14</sup> C	Radioactive decay	Q
Ar, Kr, Xe	Temperature dependence of solubility	Q <sup>+1</sup>
<sup>222</sup> Rn	Time taken to equilibrate with rock	L <sup>+2</sup>
<sup>85</sup> Kr	Radioactive decay	Q/R <sup>+3</sup>
<sup>39</sup> Ar	Radioactive decay	Q/R <sup>+3</sup>
<sup>81</sup> Kr	Radioactive decay	Q/R <sup>+3</sup>
<sup>21</sup> Ne	Accumulation from radioactive decay of U and Th	Q
<sup>4</sup> He	Accumulation from radioactive decay of U and Th	Q
U-series nuclides	Radioactive decay/time taken to equilibrate with rock	Q
<sup>129</sup> I	Radioactive decay	Q
<sup>36</sup> Cl	Radioactive decay/time taken to equilibrate with rock	Q
<sup>18</sup> O/ <sup>16</sup> O and <sup>2</sup> H/ <sup>1</sup> H	Climatic variation of recharge	R
<sup>13</sup> C/ <sup>12</sup> C	Variation with progressive water/rock interactions	R
<sup>87</sup> Sr/ <sup>86</sup> Sr	Variation with progressive rock interaction and ages of Sr-bearing minerals are known	L
Chemical evolution	Variation in concentrations with progressive water/rock interaction	R
<sup>34</sup> S/ <sup>32</sup> S	Variation with progressive water/rock interactions	R

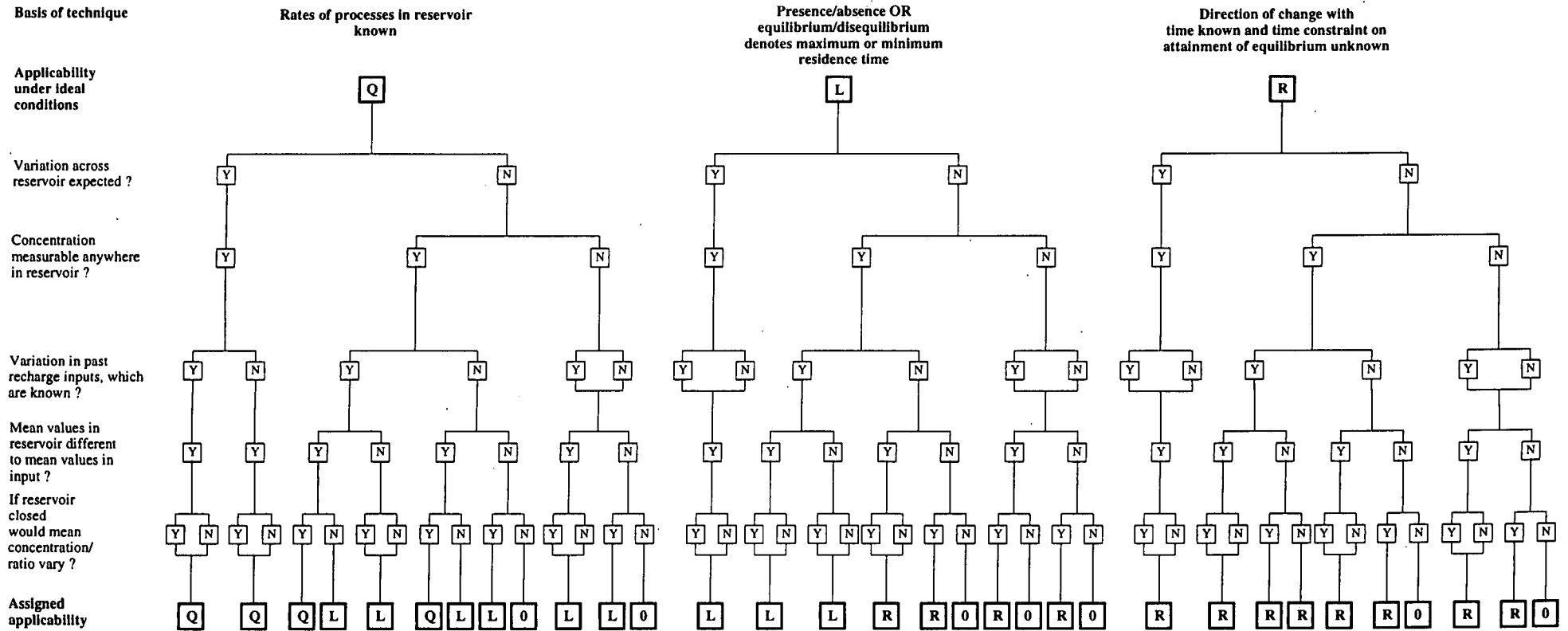
<sup>+1</sup>If the recharge temperature is estimated from these gases and then related to independent temperature versus time data, then quantitative ages may be estimated. In practice relative residence times are more likely to be estimated.

<sup>+2</sup> <sup>222</sup>Rn has a half-life of only 3.82 days and therefore usually will not give quantitative age estimates. It is more likely to be the case that the Rn has equilibrated with the formation. Such equilibration will occur if the residence times are more than a few days. Limiting residence times of this duration are likely to be of use mainly for assessing whether the act of sampling has drawn waters into the formation from elsewhere.

<sup>+3</sup> Relative residence time if *in-situ* production significant. Rates of *in-situ* production are currently unknown for these solutes.

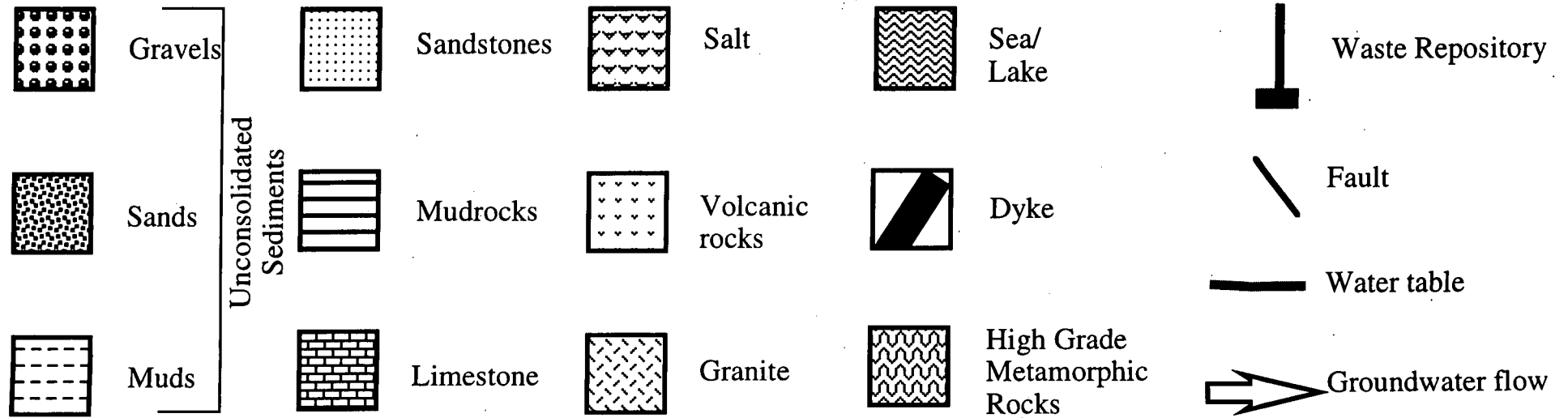
Figure 6 Scheme for assigning designations (Q, L, R, or 0) to each technique for estimating solute residence time.

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Note: A quantitative designation is given where residence time is defined according to Figure 4.

Figure 7





**Table 2** Examples illustrating the basis for assigning an ideal applicability to residence time indicators showing three different types of behaviour. The variations in these residence time indicators are illustrated schematically in Figure 8.

Reservoir		Residence Time Indicator					
		A, e.g. <sup>14</sup> C		B, e.g. <sup>4</sup> He		C, e.g. <sup>3</sup> H	
N°	Description	Variation in Reservoir	Applicability for Estimating τ	Variation in Reservoir	Applicability for Estimating τ	Variation in Reservoir	Applicability for Estimating τ
1	Sandstone above water table	Concentration constant as τ in reservoir increases (e.g. water flow through reservoir rapid of radioactive decay)	L	Concentration increase slight as τ in reservoir increases (e.g. slight increase in <sup>4</sup> He due to diffusive flux from below, from outside reservoir)	0	Concentration decreases as τ in reservoir increases	Q
2	Sandstone below water table to left of fault	Concentration decreases as τ in reservoir increases (e.g. water flow through reservoir slow of radioactive decay)	Q	Concentration increases as τ in reservoir increases (e.g. due to in-situ production of <sup>4</sup> He)	Q	Concentration zero (e.g. residence time sufficiently long for <sup>3</sup> H to have decayed below detection limit.)	L*
3	Fault zone	Concentration decreases as τ in reservoir increases	Q	Concentration constant as τ in reservoir increases (e.g. diffusive flux = in-situ radiogenic flux)	L	Concentration zero (e.g. residence time sufficiently long for <sup>3</sup> H to have decayed below detection limit.)	0*
4a 4b	Sandstone below water table to right of fault	Concentration zero (i.e. residence time sufficiently long for average <sup>14</sup> C over whole reservoir to be below detection limit)	L*	Concentration increases as τ in reservoir increases (e.g. due to in-situ production of <sup>4</sup> He)	Q	Concentration zero (e.g. residence time sufficiently long for <sup>3</sup> H to have decayed below detection limit.)	0*
5	Granite to left of fault	Concentration zero (e.g. residence time sufficiently long for <sup>14</sup> C to have decayed below detection limit.)	0*	Concentration increases as τ in reservoir increases (e.g. due to in-situ production of <sup>4</sup> He)	Q	Concentration zero (e.g. residence time sufficiently long for <sup>3</sup> H to have decayed below detection limit.)	0*
6	Shale to right of fault	Concentration zero (e.g. residence time sufficiently long for <sup>14</sup> C to have decayed below detection limit.)	0*	Concentration constant as τ in reservoir increases (e.g. diffusive flux = radiogenic flux)	L	Concentration zero (e.g. residence time sufficiently long for <sup>3</sup> H to have decayed below detection limit.)	0*

\* e.g. If inputs to a reservoir are finite but close to zero, and when averaged over the reservoir the values are effectively zero, then a limit can be placed upon the residence time of the water within the reservoir. In the sandstone to the right of the fault the majority of the water is known to originate in the sandstone to the left of the fault and this latter will contain a quantity of A (see 4a in Figure 8). Hence, the residence time of the solutes in the reservoir to the right of the fault can be fixed at a lower limit. For example, if a small quantity of <sup>14</sup>C actually enters reservoir 4, but decays within a short distance of the fault (4a), so that the reservoir effectively contains zero <sup>14</sup>C, then a lower limit can be placed upon the residence time in the reservoir. Therefore the applicability is L. In the cases of the granite and mudstone reservoirs, the water could originally have contained zero concentrations of solute A when it entered the formation. Thus, in the absence of corroborating evidence, nothing can be stated about the residence time of the solute in these formations and the applicability is 0.

### Applicability for Estimating Residence Times, τ, of Groundwaters in the Reservoirs

- Q** Quantitative residence time estimate possible
- L** Quantitative upper or lower limits can be placed upon the residence time of the solute within the reservoir
- R** Estimate of residence time relative to other solutes in the same reservoir and/or the same solute in different reservoirs
- 0** Probably inapplicable: the residence time of the solute within the reservoir cannot be estimated

### NOTE:

1. It is assumed that the solutes move at the same rate as the waters
2. Applicability to estimation of residence times is the best that can be envisaged
3. Groundwater flow paths are known and are as illustrated in the figure
4. Single solutes only considered i.e. the possibility of estimating τ for the solute of interest from τ for other solutes is not considered.

Figure 8 Schematic illustration showing the contrasting behaviours of three different groundwater residence time indicators within different rock reservoirs. See Table 2 for explanation.

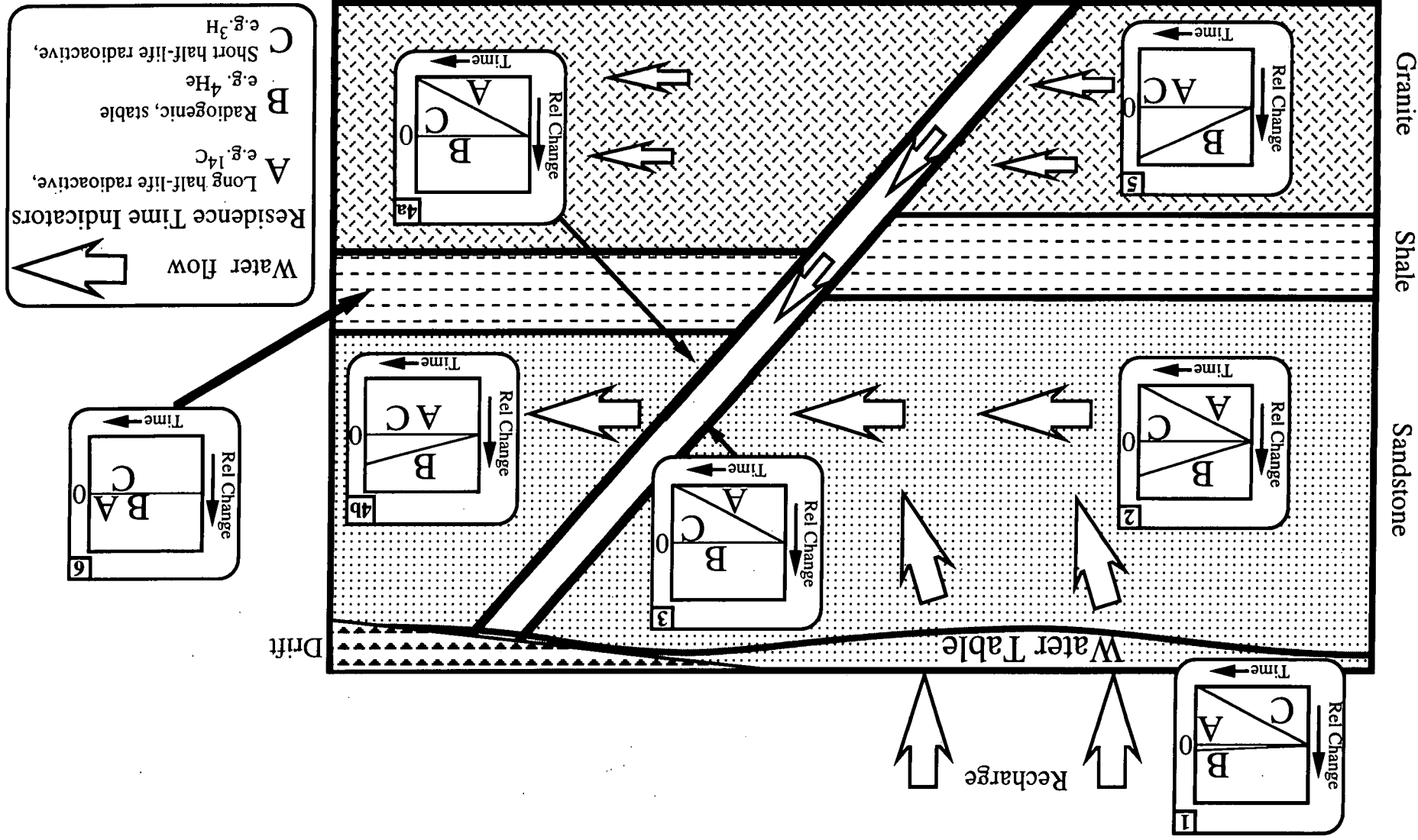


Table 3

<b>Setting:</b> Crystalline Shield Type	<b>Description:</b> A granite intrusion and dyke cut metamorphic crystalline rocks. These basement rocks are overlain by a cover of unconsolidated sediment. There is little relief and groundwater in the deep groundwaters is almost stationary. Groundwater flows through the near-surface deposits into rivers. Climate temperate. Basement Pre-Cambrian; cover Quaternary
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Reservoir			Residence Time Indicators: Most probable 'ideal' applicabilities																		
N <sup>o</sup>	Description	Origin of Water	<sup>3</sup> H	CFCs	Agri-chemicals	<sup>14</sup> C	Noble Gases						U-series Nuclides	<sup>129</sup> I	<sup>36</sup> Cl	<sup>18</sup> O/ <sup>16</sup> O and <sup>2</sup> H/ <sup>1</sup> H	<sup>12</sup> C/ <sup>13</sup> C	<sup>87</sup> Sr/ <sup>86</sup> Sr	Chemical Evolution e.g Na Conc	<sup>32</sup> S/ <sup>34</sup> S	
							Ar, Kr, Xe Solubility	<sup>222</sup> Rn	<sup>85</sup> Kr	<sup>39</sup> Ar	<sup>21</sup> Ne	<sup>4</sup> He									<sup>81</sup> Kr
1	Unconsolidated sediments above water table	Rainfall	Q	Q	L	Q	L	L	Q	Q	0	0	Q	0	Q	Q	R	R	L	R	R
2	Unconsolidated sediments below water table	Water from above water table	Q	Q	L	Q	Q	L	L	Q	Q	Q	Q	Q	Q	Q	R	R	L	R	R
3	Granite below water table	Basement	0	0	0	0	0	L	R	R	L	L	L	Q	L	L	0	R	L	0	R
4	Fault zone below water table	Basement	0	0	0	0	0	L	R	R	L	L	L	Q	L	L	0	R	L	0	R
5	Crystalline rock below the water table	Basement	0	0	0	0	0	L	R	R	L	L	L	Q	L	L	0	R	L	0	R
6	Dyke below water table	Basement	0	0	0	0	0	L	R	R	L	L	L	Q	L	L	0	R	L	0	R

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**Effect of Climate change**  
The most likely effect is that the water table will move upwards or downwards (depending upon whether or not rainfall increases or decreases). In other words, Reservoirs (1) and (2) will increase or decrease in size.

**General Comments**  
'Basement' water origin means water has approached equilibrium with basement rocks for a significant number of solutes. Effectively, groundwater in the basement is stationary on the timescale of interest to radioactive waste studies. Different rocks have different production rates of <sup>4</sup>He, <sup>81</sup>Kr etc. Water crosses sediments rapidly of time for tritium decay to zero.

**Applicability**  
**Q** Quantitative  
**L** Quantitative limits  
**R** Relative only  
**0** Probably Inapplicable

Figure 9 The Crystalline Shield Type reference hydrogeological environment.

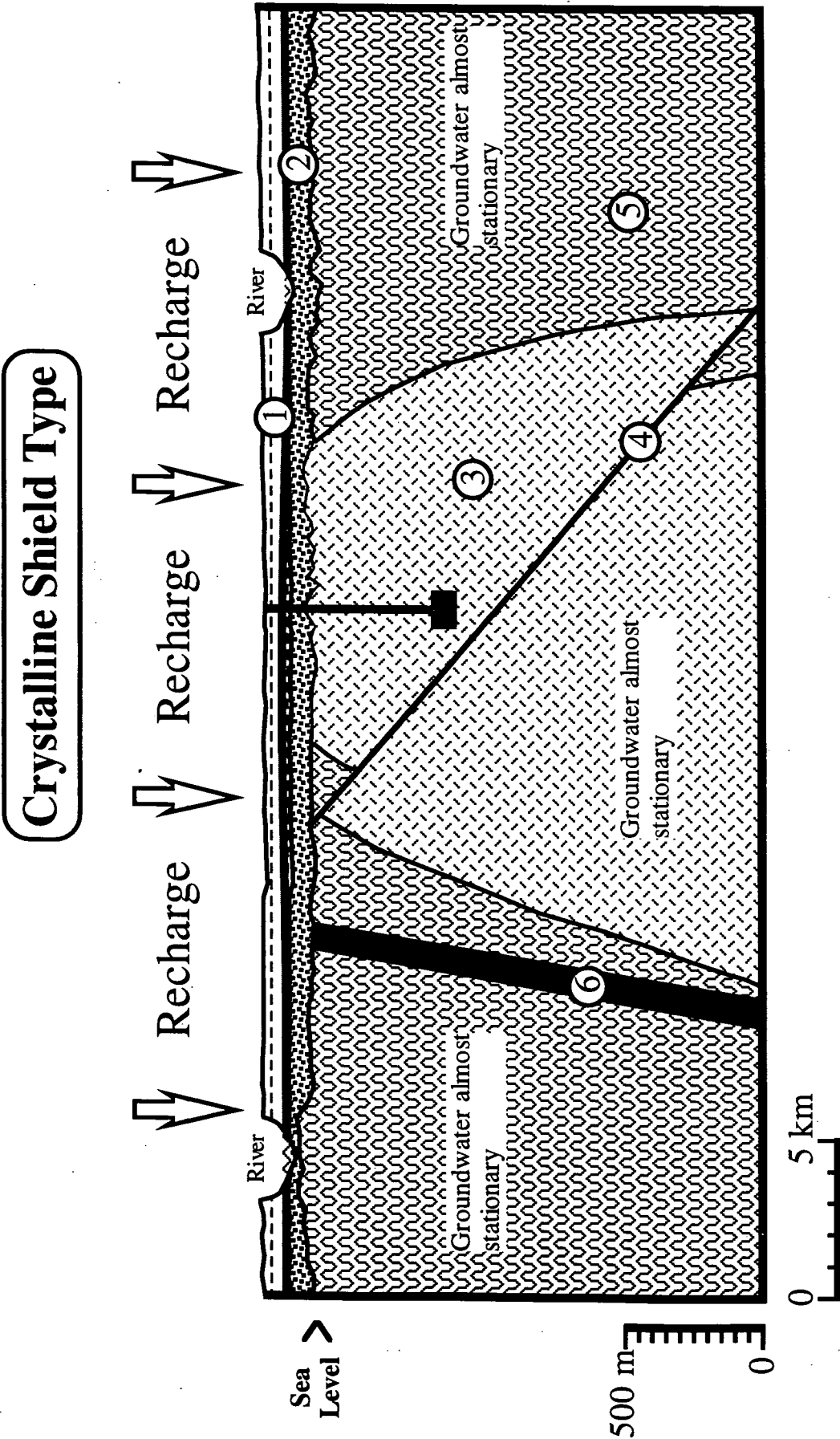


Table 4

Setting: Argillaceous rock beneath low-lying plain	Description: Gently dipping interlayered clays and sands overlying limestone. Dominant water flow is from recharge down-dip. Clays act as aquicludes with little water movement, although some water may move vertically. Climate temperate. Limestone Carboniferous; Shales and sandstones Tertiary.
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Reservoir			Residence Time Indicators: Most probable 'ideal' applicabilities																		
N <sup>o</sup>	Description	Origin of Water	Noble Gases											U-series Nuclides	129I	36Cl	18O/16O and 2H/1H	12C/13C	87Sr/86Sr	Chemical Evolution e.g. Na concn	32S/34S
			3H	CFCs	Agri-chemicals	14C	Ar, Kr, Xe Solubility	222Rn	85Kr	39Ar	21Ne	4He	81Kr								
1	Sediments in unsaturated zone	Rainfall	Q	Q	L	Q	L	L	Q	Q	0	0	Q	0	Q	Q	R	R	L	R	R
2	Sandstone aquifers below water table	Water from above water table	L	L	L	Q	Q	L	L	Q	Q	Q	Q	Q	Q	Q	R	R	L	R	R
3	Clay aquicludes below water table	Water from deep aquifers	0	0	0	L	L	L	L	L	Q	Q	Q	Q	Q	Q	R	R	L	R	R
3a	Clay aquiclude below sea bed	Sea and aquifer	0	0	0	L	L	L	L	L	Q	Q	Q	Q	Q	Q	R	R	L	R	R
4	Limestone aquifer below water table	Water from above water table	L	L	L	Q	Q	L	L	L	Q	Q	Q	Q	Q	Q	R	R	R	R	R

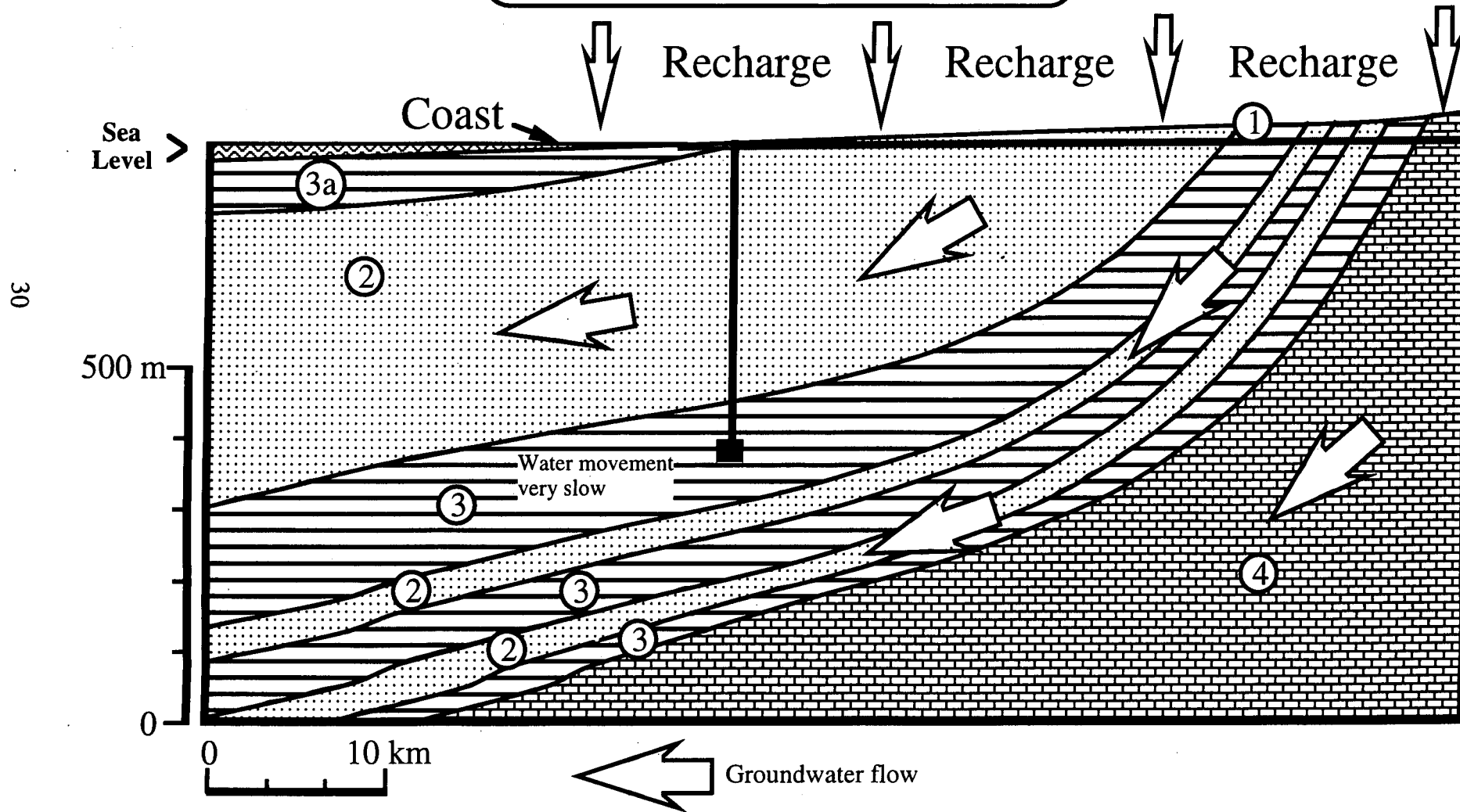
**Effect of Climate change**  
 More rainfall or meltwater from glacial sheets would enhance recharge and reduce residence times in Reservoirs (2) and (4). Sea-level rise would promote saline intrusion into (2). Climate change would probably have less effect in the less-permeable Reservoir (3).

**General Comments**  
 Sandstone and limestone aquifers are similar. More rapid flow means shorter-lived indicators can be used. These are of less use in mudrocks. Longer-lived indicators of little use in unsaturated zone. Complete exchange of water and solutes between aquifer and aquicludes occurs on time scale of 10's of thousands of years.

**Applicability**  
**Q** Quantitative  
**L** Quantitative limits  
**R** Relative only  
**0** Probably Inapplicable

Figure 10 The Argillaceous Rock Beneath Low-lying Plain Type reference hydrogeological environment.

**Argillaceous Rock Beneath  
Low-lying Plain Type**



# Table 5

<b>Setting:</b> Coastal, Basin Margin Type	<b>Description:</b> Crystalline basement (of granite and volcanic rocks), is overstepped by a sedimentary sequence that thickens towards the left of the diagram. The basin margin is faulted. Water flows from upland areas towards the left. Smaller movements of groundwater also occur from the granite, and the sedimentary basin. Climate is temperate. Granite and volcanics are of early Palaeozoic age; sedimentary rocks of cover are of Mesozoic age
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Reservoir			Residence Time Indicators: Most probable 'ideal' applicabilities																		
N <sup>o</sup>	Description	Origin of Water	<sup>3</sup> H	CFCs	Agri-chemicals	<sup>14</sup> C	Noble Gases						U-series Nuclides	<sup>129</sup> I	<sup>36</sup> Cl	<sup>18</sup> O/ <sup>16</sup> O and <sup>2</sup> H/ <sup>1</sup> H	<sup>12</sup> C/ <sup>13</sup> C	<sup>87</sup> Sr/ <sup>86</sup> Sr	Chemical Evolution e.g. Na concn	<sup>32</sup> S/ <sup>34</sup> S	
							Ar, Kr, Xe Solubility	<sup>222</sup> Rn	<sup>85</sup> Kr	<sup>39</sup> Ar	<sup>21</sup> Ne	<sup>4</sup> He									<sup>81</sup> Kr
1	Volcanic rock above water table	Rainfall	Q	Q	L	Q	L	L	Q	Q	0	0	Q	0	Q	Q	R	R	L	R	R
2	Volcanic rock below water table	Water from above water table	L	L	L	Q	Q	L	L	Q	Q	Q	Q	Q	Q	Q	R	R	L	R	R
3	Granite basement below water table	Deeper granite	0	0	0	0	0	L	R	R	Q	Q	Q	Q	L	L	0	0	L	0	0
4	Basin margin fault in basement. Water flows across fault	Volcanic basement	0	0	0	0	0	L	0	0	L	L	L	L	0	0	0	R	L	0	R
5	Sandstone forming basin fill	Sedimentary basinal brine	0	0	0	0	0	L	R	R	Q	Q	Q	Q	L	L	0	0	L	0	0

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**Effect of Climate change**  
 If the climate became more arid, and /or sealevel falls, then the water table may depress and near-surface reservoirs (represented by Reservoir (1)) would increase in volume. The water in Reservoir (5) might move towards the right in this case. More rainfall and/or sealevel rise would lead to the reverse changes.

**General Comments**  
 The residence times of solutes in the faults are very difficult to determine because the water flows across the faults. Hence, waters are resident in the fault zones for relatively short periods of time.

- Applicability**
- Q** Quantitative
  - L** Quantitative limits
  - R** Relative only
  - 0** Probably Inapplicable

Figure 11 The Coastal, Basin Margin Type reference hydrogeological environment.

# Coastal, Basin Margin Type

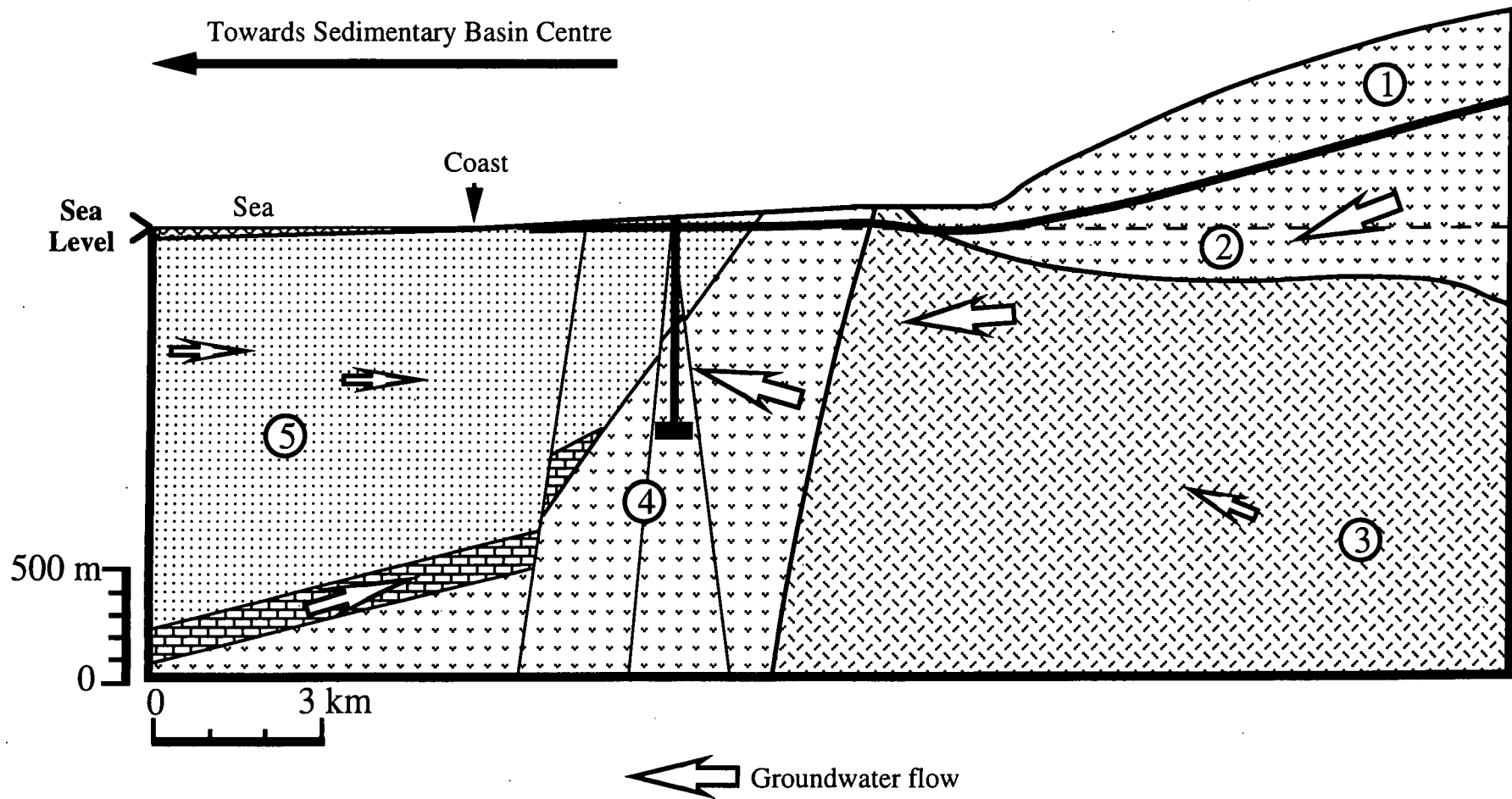




Table 6

<b>Setting:</b> Salt Dome Beneath Low-Lying Plain Type	<b>Description:</b> A mudrock sequence intruded by a salt diapir is overlain unconformably by unconsolidated sediments. Most groundwater flow takes place sub-horizontally through these sediments on a regional scale, with only minor upflow from mudrocks. Climate temperate. Unconsolidated sediments Quaternary; sedimentary rocks Tertiary.
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Reservoir			Residence Time Indicators: Most probable 'ideal' applicabilities																		
N°	Description	Origin of Water	Noble Gases											U-series Nuclides	129I	36Cl	18O/16O and 2H/1H	12C/13C	87Sr/86Sr	Chemical Evolution e.g. Na concn	32S/34S
			3H	CFCs	Agri-chemicals	14C	Ar, Kr, Xe Solubility	222Rn	85Kr	39Ar	21Ne	4He	81Kr								
1	Sediments within the unsaturated zone	Rainfall	Q	Q	L	Q	L	L	Q	Q	0	0	Q	0	Q	Q	R	R	L	R	R
2	Unconsolidated deposits of muds, sands and gravels	Water from above water table	Q	Q	L	Q	L	L	Q	Q	0	0	Q	L	L	Q	R	R	L	R	R
3	Mudrocks intruded by salt diapir. Water stationary	Unknown. Negligible input from surrounding formation	0	0	0	0	0	L	R	R	Q	Q	Q	Q	Q	L	R	R	L	0	0
4	Water in and around the edge of salt diapir. Water stationary	Deeper formations-displaced by diapir	0	0	0	0	0	L	R	R	Q	Q	Q	Q	Q	L	0	R	L	0	0

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**Effect of Climate change**  
Sea-level change due to glacial-interglacial conditions, and to a lesser extent arid-pluvial conditions, could result in water level changes, creating or eliminating a significant Reservoir (1). Ice loading or permafrost might isolate Reservoir (1) from the atmosphere, while ice-damming could create surface water with no Reservoir (1).

**General Comments**  
Reservoir (1) consists of a wide variety of sediment types and the assessment of residence time indicators is biased towards sands and gravels, which will have higher transmissivities. Effectively, weighted average residence times are indicated. Reservoir (3) is a volumetrically small reservoir, but may contain long residence waters and solutes.

**Applicability**  
**Q** Quantitative  
**L** Quantitative limits  
**R** Relative only  
**0** Probably Inapplicable

Figure 12 The Salt Dome Beneath Low-lying Plain Type reference hydrogeological environment.

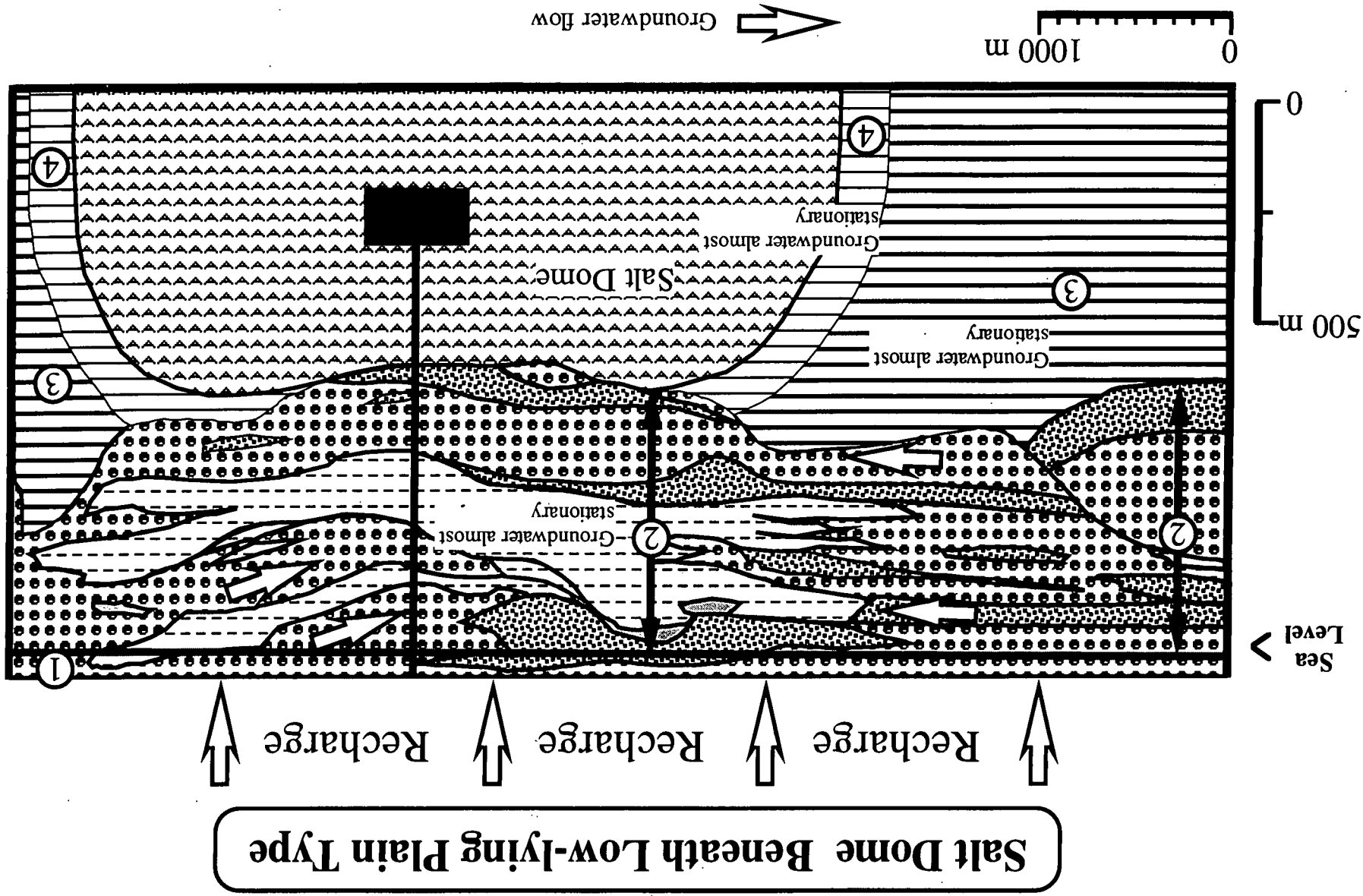


Table 7

<b>Setting:</b> Basin and range type	<b>Description:</b> Fault-bounded ridges and basins occur in a volcano-sedimentary sequence. Recharge is limited. Groundwater flows towards basin centres. Contrasting flow regimes occur in 'stacked' aquifers. The tuff is recharged locally; the deeper aquifer is recharged some distance away. Climate is arid. Limestone/Sandstone are Carboniferous; volcanics and dyke are Tertiary.
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Reservoir			Residence Time Indicators: Most probable 'ideal' applicabilities																						
N°	Description	Origin of Water	Noble Gases															U-series Nuclides	129I	36Cl	18O/16O and 2H/1H	12C/13C	87Sr/86Sr	Chemical Evolution e.g. Na concn	32S/34S
			3H	CFCs	Agri-chemicals	14C	Ar, Kr, Xe Solubility	222Rn	85Kr	39Ar	21Ne	4He	81Kr												
1	Tuff above water table. Limited recharge	Rainfall	Q	Q	0	Q	L	L	Q	Q	0	0	Q	0	Q	Q	R	R	L	R	R				
2	Tuff below water table	Water from above water table-local recharge	L	L	0	Q	Q	L	L	Q	Q	Q	Q	Q	Q	Q	R	R	L	R	R				
3	Basaltic dyke cutting shallow and deep aquifers	Deep aquifer flow system	0	0	0	L	L	L	R	R	Q	Q	Q	Q	Q	Q	0	0	L	R	R				
4	Deep carbonate/sandstone aquifer	Meteoric recharge some distance away	L	L	0	Q	Q	L	L	L	Q	Q	Q	Q	Q	Q	R	R	R	R	R				
5	Fault within tuffs	Shallow and deep flow systems	0	0	0	L	L	L	R	R	R	R	Q	L	L	L	0	R	L	R	R				

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**Effect of Climate change**

Increases in rainfall may lead to the water table rising and the expansion of Reservoir (2) and contraction of Reservoir (1). Increases in rainfall may also increase the potential for waters to ascend the faults in the area. A decrease in rainfall may lead to cross-flows of water between formations diminishing, depending upon the effect on the different recharge zones.

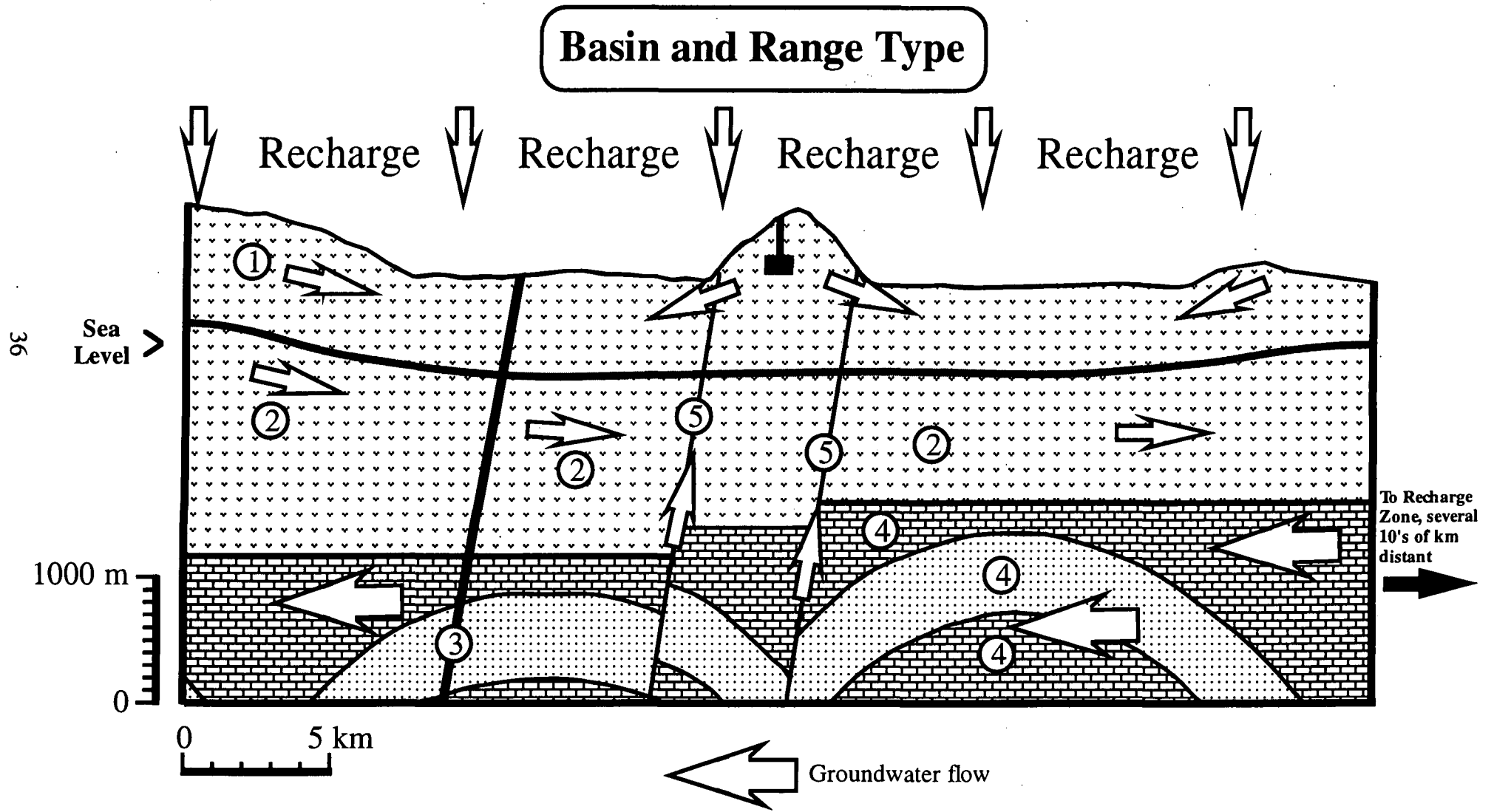
**General Comments**

The precise application of groundwater dating techniques to Reservoir (4) is dependent upon this reservoir being connected directly to the zone of recharge (e.g. detectable levels of 14C occur in this reservoir near recharge). If recharge to this reservoir diminished, then certain techniques may become inapplicable. Agri-chemicals are unlikely to be useful in an arid climate

**Applicability**

- Q** Quantitative
- L** Quantitative limits
- R** Relative only
- 0** Probably Inapplicable

Figure 13 The Basin and Range Type reference hydrogeological environment.



<b>Setting:</b> Argillaceous rocks in Foreland Basin	<b>Description:</b> Strongly folded Mesozoic sediments emplaced as nappes over Lower Palaeozoic crystalline basement. Folding Tertiary Groundwater moves down-dip due to topographic drive, along the more permeable sediments. The area is tectonically active and regularly spaced vertical fractures may act as fluid conduits.
--	--

Reservoir		Residence Time Indicators: Most probable 'ideal' applicabilities																			
N <sup>o</sup>	Description	Origin of Water	<sup>3</sup> H	CFCs	Agri-chemicals	<sup>14</sup> C	Noble Gases						U-series Nuclides	<sup>129</sup> I	<sup>36</sup> Cl	<sup>18</sup> O/ <sup>16</sup> O and <sup>2</sup> H/ <sup>1</sup> H	<sup>12</sup> C/ <sup>13</sup> C	<sup>87</sup> Sr/ <sup>86</sup> Sr	Chemical Evolution e.g Na Conc	<sup>32</sup> S/ <sup>34</sup> S	
							Ar, Kr, Xe Solubility	<sup>222</sup> Rn	<sup>85</sup> Kr	<sup>39</sup> Ar	<sup>21</sup> Ne	<sup>4</sup> He									<sup>81</sup> Kr
1	Unsaturated zone and surface layers including unconsolidated landslip	Rainfall	Q	Q	0	Q	L	L	Q	Q	0	0	Q	0	Q	Q	R	R	L	R	R
2	Permeable limestone layers below water table hydraulically connected to surface	Mainly from above water table. Some from (5)	L	Q	0	Q	Q	L	L	Q	Q	Q	Q	Q	Q	Q	R	R	R	R	R
3	Poorly permeable marls below water table	Mainly from adjacent formations	0	0	0	L	0	L	0	L	Q	Q	Q	Q	Q	Q	R	R	R	R	R
4	Crystalline fractured basement. Water stationary	'Basement' Water unrelated to recent recharge	0	0	0	0	0	L	R	R	Q	Q	Q	Q	Q	L	0	R	L	R	0
5	Intensely folded sandstones and shales. Low groundwater flows	Sediment dewatering at greater depth	0	0	0	0	0	L	R	R	Q	Q	Q	Q	L	L	0	R	L	R	R
6	Fracture systems which may act as conduits for upward water flow	Surrounding formations	0	0	0	0	L	L	R	R	R	R	Q	L	L	L	0	R	L	R	R

**Effect of Climate change**

Covering by ice will affect recharge and residence times in Reservoirs (1), (2) and (6). Arid conditions would lead to an increase in the volume of Reservoir (1). Sea level change would have little effect due to the elevation.

**General Comments**

Relief makes agriculture and therefore agrichemical input minor. For basement rocks, only methods based on in situ production + Water/Rock Interaction can be used. Other reservoirs may contain recent recharge so other methods can be used as well.

**Applicability**

- Quantitative  
 Quantitative limits  
 Relative only  
 Probably Inapplicable

Figure 14 The Argillaceous Rock in Foreland Basin Type reference hydrogeological environment.

### Argillaceous Rock in Foreland Basin Type

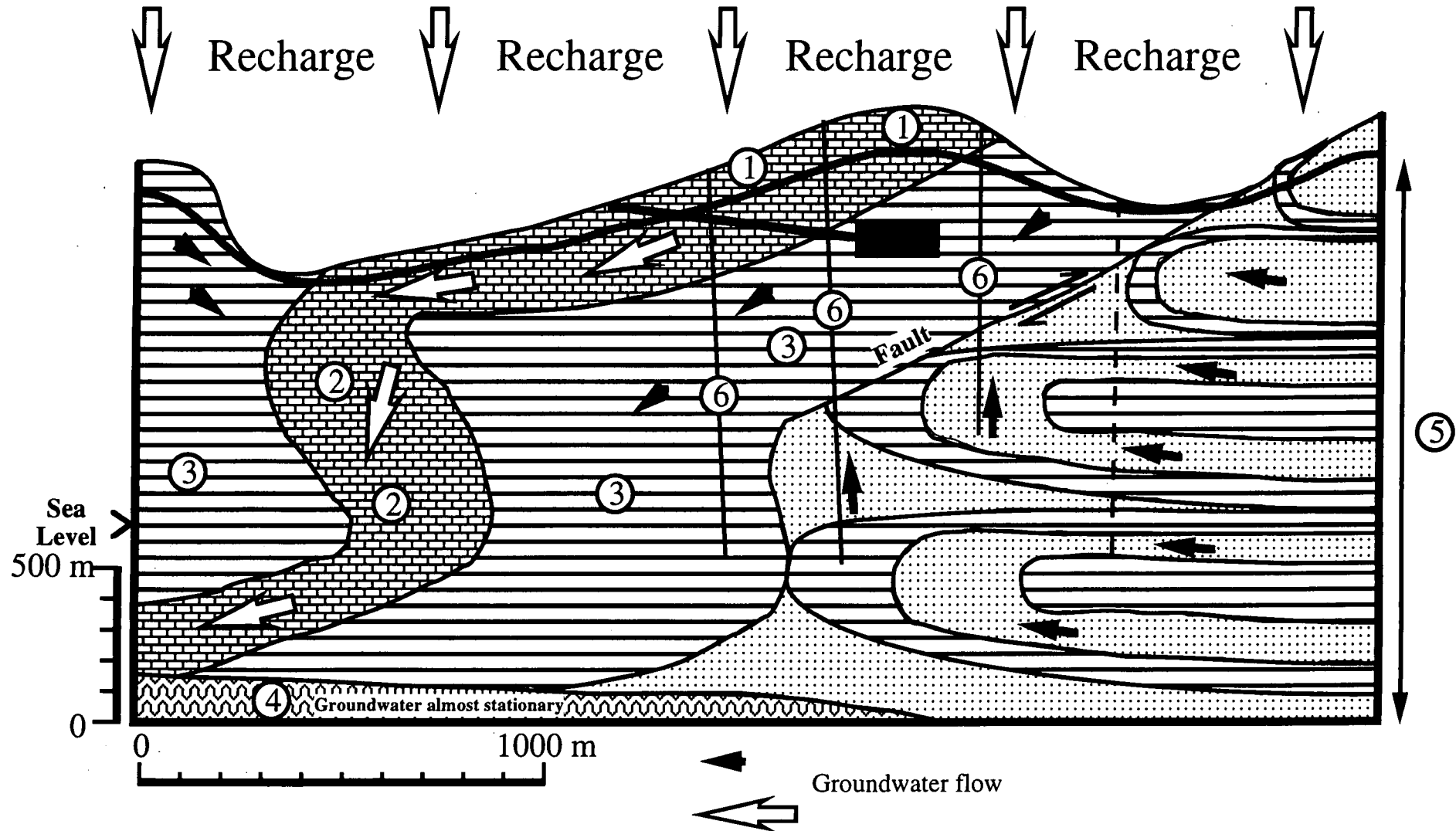


Table 9

<b>Setting:</b> Sedimentary Basin at a Destructive Plate Margin Type	<b>Description:</b> An intermontane basin containing Quaternary sediments is underlain by a Mesozoic granitic basement. The area is undergoing rapid uplift. A shallow groundwater flow system, driven by local topographical variations, occurs above a deeper regional flow system. The basin is faulted and water flows upwards along the faults owing to pressure release as a result of unloading during uplift. The climate is temperate.
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Reservoir			Residence Time Indicators: Most probable 'ideal' applicabilities																		
N°	Description	Origin of Water	<sup>3</sup> H	CFCs	Agri-chemicals	<sup>14</sup> C	Noble Gases							U-series Nuclides	<sup>129</sup> I	<sup>36</sup> Cl	<sup>18</sup> O/ <sup>16</sup> O and <sup>2</sup> H/ <sup>1</sup> H	<sup>12</sup> C/ <sup>13</sup> C	<sup>87</sup> Sr/ <sup>86</sup> Sr	Chemical Evolution e.g. Na concn	<sup>32</sup> S/ <sup>34</sup> S
							Ar, Kr, Xe Solubility	<sup>222</sup> Rn	<sup>85</sup> Kr	<sup>39</sup> Ar	<sup>21</sup> Ne	<sup>4</sup> He	<sup>81</sup> Kr								
1	Unconsolidated sediment above water table	Rainfall	Q	Q	L	Q	L	L	Q	Q	0	0	Q	Q	Q	Q	R	R	L	R	R
2	Granitic rock. Affected by deep flow system	Water from above water table	L	L	L	L	Q	L	R	R	Q	Q	Q	Q	Q	Q	R	R	L	R	R
3	Fault within intermontane basin. Water flows up fault	Surrounding formations	0	0	0	0	L	L	R	R	R	R	R	L	L	L	R	R	L	R	R
4	Sandstone in sedimentary basin. Affected by deep flow system	Meteoric recharge some distance away	0	0	0	0	L	L	R	R	Q	Q	Q	Q	Q	Q	R	R	L	R	R
5	Granitic rock below water table. Affected by shallow flow system	Water from above water table	L	L	L	Q	Q	L	R	R	Q	Q	Q	Q	Q	Q	R	R	L	R	R

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**Effect of Climate change**  
 If the climate became more arid then the water table may be depressed and near-surface reservoirs (represented by Reservoir (1)) would increase in volume. More rainfall would lead to the reverse changes.

**General Comments**  
 The residence times of solutes in the faults can be evaluated because water flow occurs along the fault, and water passes through different lithologies.

**Applicability**  
**Q** Quantitative  
**L** Quantitative limits  
**R** Relative only  
**0** Probably Inapplicable

Figure 15 The Sedimentary Basin at a Destructive Plate Margin Type reference hydrogeological environment.

