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UNCONSOLIDATED SEDIMENTARY AQUIFERS : REVIEW NO 8 - ISOTOPE HYDROLOGY

W G Darling



International Division
British Geological Survey
Keyworth
Nottingham
United Kingdom NG12 5GG



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Sigatoka River flood plain, Fiji

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Unconsolidated Sedimentary Aquifers

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A Guide to the sedimentology of unconsolidated sedimentary aquifers (UNSAs)

INTRODUCTION

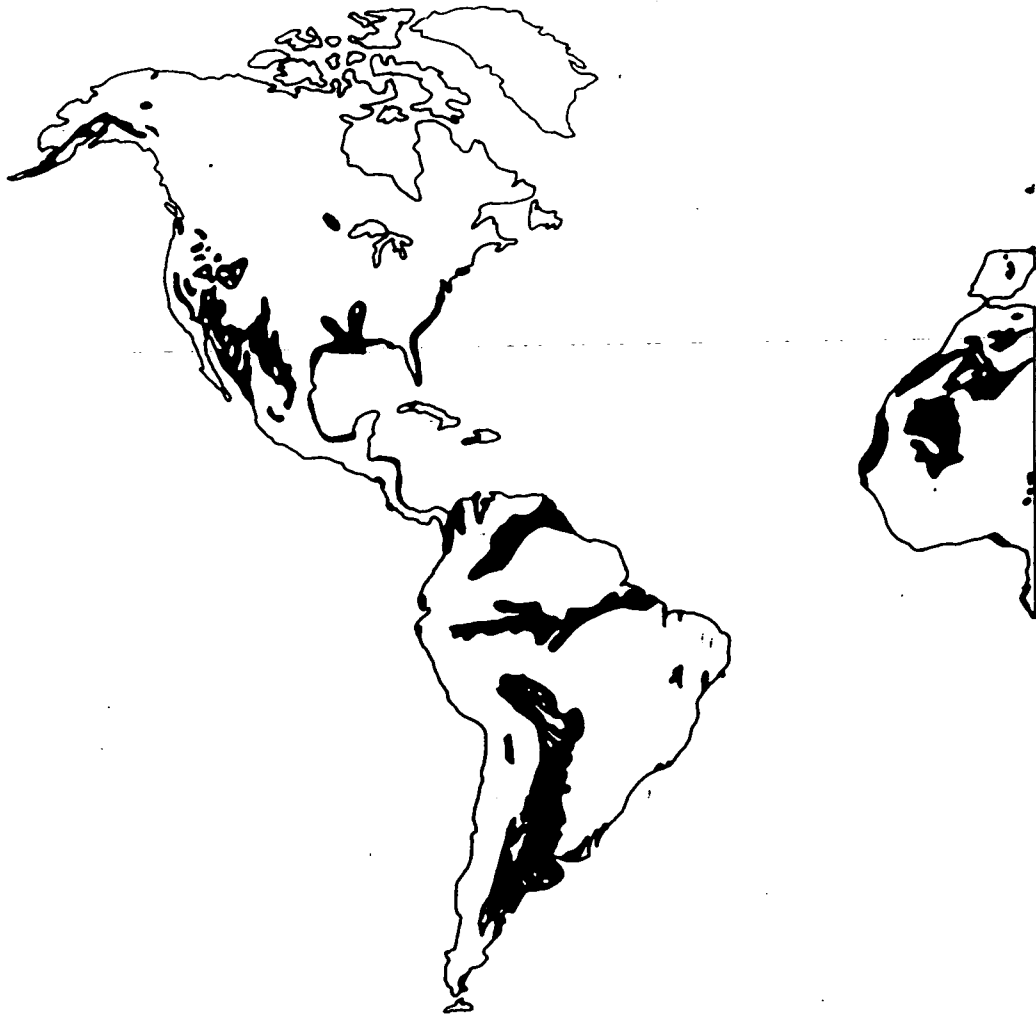
WHAT ARE UNSAs AND WHY IS IT IMPORTANT TO UNDERSTAND THEM?

UNSAs are unconsolidated sedimentary aquifers. These are the water-bearing strata within the swathes of unconsolidated sediment that mantle much of the earth's surface. There is no clear dividing line between UNSAs and aquifers in consolidated rocks, as lithification is a gradational process: deposits a hundred years old can be lithified, while some deposits 500 million years old are still essentially unlithified. However, for most purposes, UNSAs can be understood as deposits which have accumulated over the past few million years, that is during Quaternary and Neogene (late Tertiary) time. They are important sources of water in many parts of the world, and in particular constitute the only major sources of groundwater for vast areas throughout the developing world. In the influential text-book *Hydrogeology* by Davies and De Weist it says:

"The search for ground water most commonly starts with an investigation of nonindurated sediments. There are sound reasons for this preference. First, the deposits are easy to drill or dig so that exploration is rapid and inexpensive. Second, the deposits are most likely to be found in valleys where ground-water levels are close to the surface and where, as a consequence, pumping lifts are small. Third, the deposits are commonly in a favourable location with respect to recharge from lakes and rivers. Fourth, nonindurated sediments have generally higher specific yields than other material. Fifth, and perhaps most important, permeabilities are much higher than other natural materials with the exception of some recent volcanic rocks and cavernous limestones."

To date, though, few attempts have been made to understand the detailed internal structure of unconsolidated aquifers even though such knowledge may be crucial to the long term success of any water development project. This shortcoming is probably the reason why the operational lives of many water boreholes are frequently much shorter than expected.

Understanding of the internal structure or "architecture" of many types of sedimentary deposit has, however, advanced greatly over the past couple of decades. Part of this research has been academic, but much has been sponsored by the oil industry, so as to better predict the possible location of oil within sedimentary traps. Oil, like water, is most profitably located within bodies of relatively coarse-grained and porous sediment. Thus, there is obvious scope for applying this recently gained understanding to hydrogeological problems. Advances have also been made in the understanding of the geometry of complex "soft-rock" deposits by the application of appropriate combinations of investigative techniques, including remote sensing, rapid geophysical methods and new drilling techniques. The combination of these bodies of knowledge can provide a framework for locating and assessing UNSAs.



MAJOR AREAS OF UNCONSOLIDATED SEDIMENTARY AQUIFERS WORLDWIDE

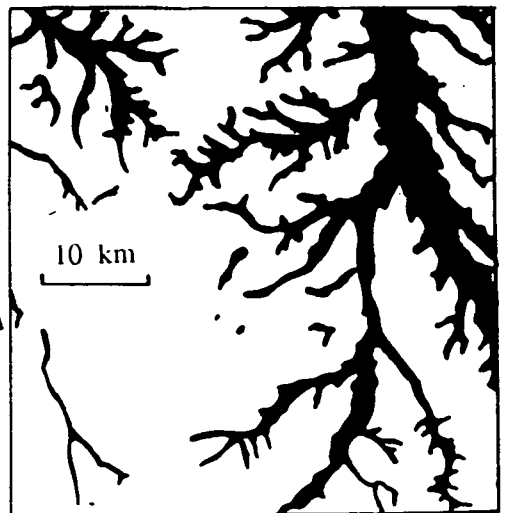
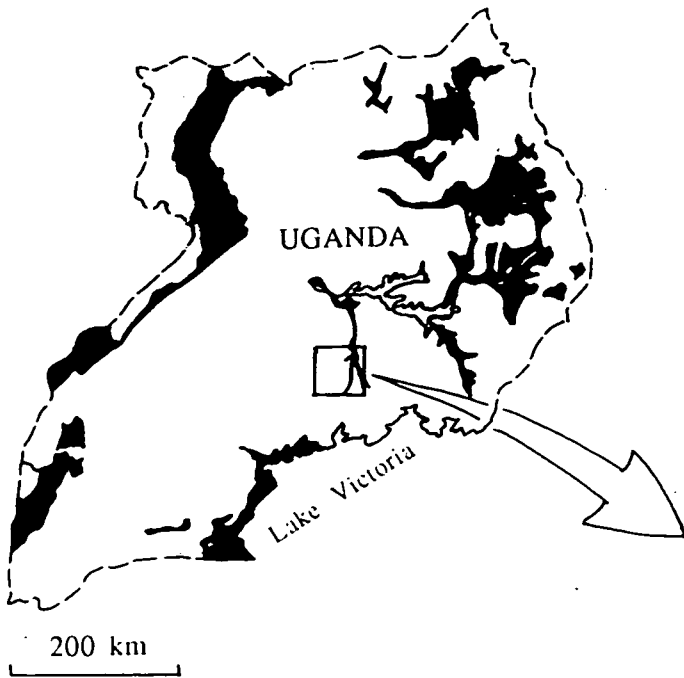
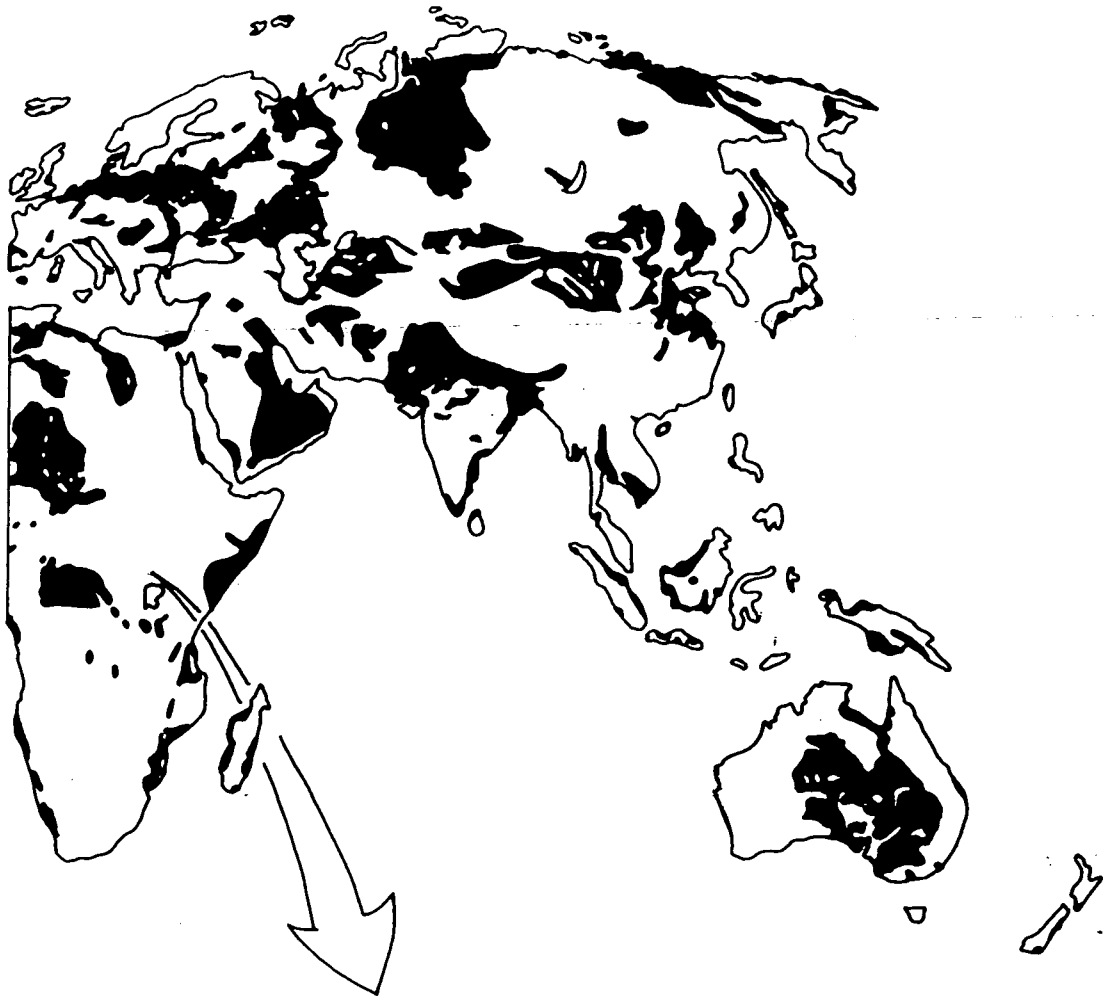
- The map shows the distribution of the thickest and most extensive Quaternary deposits in the world. The great majority of these are unconsolidated, and many include water-bearing deposits (UNSA's).

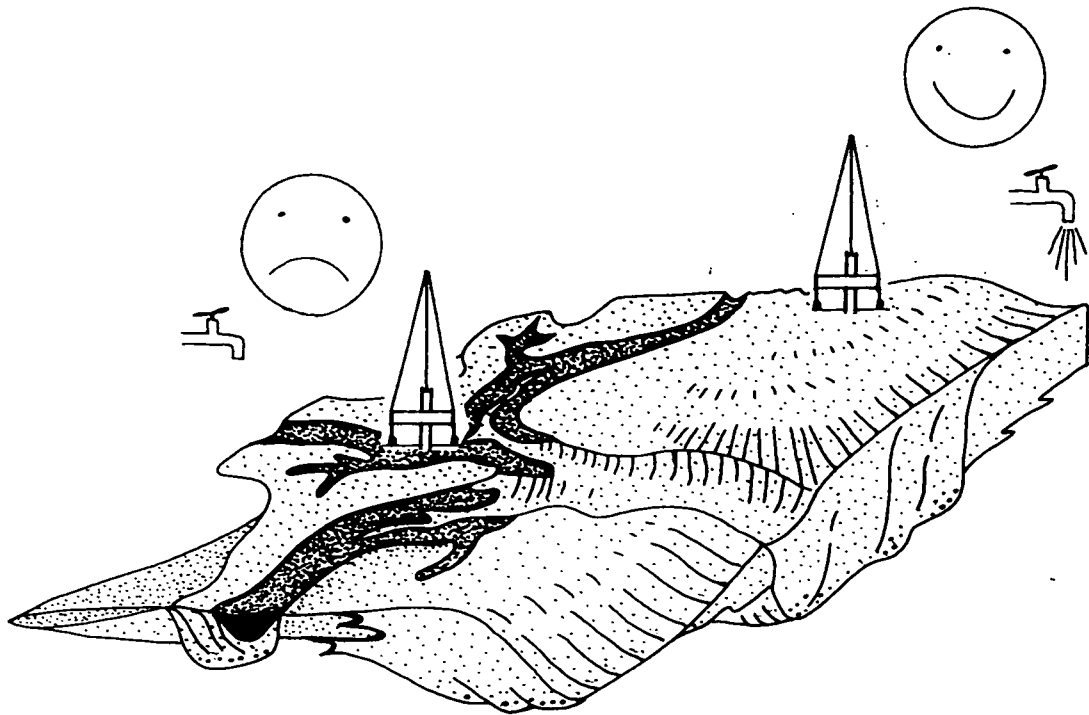
- A generalised world map such as this, though, severely under-estimates the true extent of UNSA's worldwide. This is because:

- unconsolidated pre-Quaternary deposits are omitted; these too have a wide distribution, though are difficult to delineate (as they grade into consolidated deposits); they too can include significant UNSA's.

- the simplification of linework necessary at this scale means that a large proportion of unconsolidated deposits have had to be omitted. The inset map shows the example of Uganda, which seems to have no unconsolidated sediments at the global scale, while significant and extensive deposits 'appear' once the country is looked at more closely. At a yet larger scale the unconsolidated sediments appear yet more widespread. The message is clear. *Unconsolidated sediments, and therefore UNSA's, are ubiquitous.*

Diagram data modified from various sources.





Sedimentary bodies are characterised by variably complex geometry and internal structure. These properties exert a strong internal control on the location, quantity and quality of groundwater. Diagram adapted from Galloway and Hobday (1983).

ISOTOPE HYDROLOGY

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1. AIMS

The use of isotopic methods in evaluating the hydrogeology of UNSAs is primarily based on what they can reveal about physical processes undergone by groundwaters, rather than their chemical evolution. Thus isotopic investigations tend to rely on the stable isotope ratios $^{18}\text{O}/^{16}\text{O}$ and $^2\text{H}/^1\text{H}$ as natural tracers of water sources, and the activities of the radioisotopes ^3H and ^{14}C as indicators of residence time. The stable isotope ratio $^{13}\text{C}/^{12}\text{C}$ has also been used, but mainly as an adjunct to the modelling of ^{14}C data to give groundwater 'ages'. Collectively, the above tend to be referred to as 'environmental isotopes'.

The aim of this review is to describe briefly each of the isotopes, to explain the theory behind their use in hydrogeology, and to consider the results of a variety of case histories where one or more of the isotopes has been used.

2. BACKGROUND

The stable isotopes of oxygen and hydrogen consist of a majority light isotope accompanied by varying amounts of a minority heavy isotope (isotopes are atoms with the same electron configuration and therefore chemical properties, but with differing numbers of neutrons and therefore small physical differences). Thus in the case of oxygen the average terrestrial composition is ^{16}O at 99.76% and ^{18}O at 0.20%, while for hydrogen the composition is ^1H at 99.984% and ^2H (sometimes referred to as deuterium or D) at 0.016% (Hoefs, 1987). At natural abundances, stable isotope ratios are always measured in terms of their differences from the above ratios, which are assigned to a specially-prepared sea water standard (Standard Mean Ocean Water, or SMOW) supplied by the International Atomic Energy Agency (IAEA) to isotope laboratories worldwide.

This has resulted in the δ -scale, where δ is measured in permil and defined as follows:

$$\delta = [(R_x - R_s)/R_s] \times 10^3$$

where $R_x = ^{18}\text{O}/^{16}\text{O}$ or $^2\text{H}/^1\text{H}$ in the sample
 $R_s = ^{18}\text{O}/^{16}\text{O}$ or $^2\text{H}/^1\text{H}$ in the standard

Since isotope ratio analysis by mass spectrometry is an extremely precise measurement, and since virtually all stable isotope laboratories use SMOW and the subsidiary SLAP standards for normalisation, results from different laboratories are more-or-less interchangeable and can be taken at face value with some confidence.

As stated earlier, ratios of light to heavy isotopes are primarily modified by physical processes. These may occur before or after the precipitation process. For example, when clouds pass over a mountain barrier, by the time the upper regions are reached there may have been considerable rainfall at lower altitudes. Since water molecules containing atoms of ^{18}O and/or ^2H tend to fall out first because

they are slightly heavier, this results in a general decrease in $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values with altitude. This effect is important in tracing water origins in areas of high relief.

An important post-precipitation change in $\delta^{18}\text{O}$ and $\delta^2\text{H}$ occurs when water resides at the surface for sufficient length of time to allow evaporation to occur. Under these conditions, molecules containing, ^{18}O and/or ^2H tend to be slightly more resistant to evaporation than 'ordinary' H_2O , with the result that $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values in the residual waters increase. Such a process tends to affect stream and lake waters, both of which can in certain circumstances contribute to the recharge of groundwater. The process is of particular importance in hot and arid climates, where UNSAs may form important water resources.

In general for O and H stable isotopes, evaporative effects may be distinguished from rainout effects by plotting $\delta^2\text{H}$ versus $\delta^{18}\text{O}$ values and relating the data points to the local 'meteoric line', which is the regression line for local rainfall samples, and which will usually have a high correlation coefficient. In the absence of such data, and particularly in more humid areas, the 'world meteoric line' of Craig (1961) is often a good approximation and has the form: $\delta^2\text{H} = 8 \delta^{18}\text{O} + 10$. The intercept value of 10 is sometimes known as the 'd' excess; and may vary from this figure for local meteoric lines. Basically, variations along the meteoric line tend to be related to differences in recharge altitude, while data points falling to the right of the line are due to evaporative or seawater mixing processes. However, interpretation can frequently be more complicated than this, and a fuller discussion can be found in Fritz and Fontes (1980) and IAEA (1981).

The isotopes ^{14}C (radiocarbon) and ^3H (tritium) are far less common than even the minor stable isotopes, but have the advantage of radioactivity which means they can be measured by relatively simple counting methods, albeit accompanied by much more serious potential contamination problems than the stable isotopes. For radiocarbon, measurements of ^{14}C disintegrations per minute per gram of carbon can be translated into activity of ^{14}C ($A^{14}\text{C}$), usually expressed in terms of 'percent modern carbon' (pmc), though sometimes referred to as ' $\delta^{14}\text{C}$ ' using the same expression as for stable isotopes above, but substituting $A^{14}\text{C}$ for the isotope ratios (the 'reference' value will normally be 100 pmc).

Tritium is measured in a similar way, but is expressed in tritium units (TU) or, more correctly, as tritium ratio (TR), which in both cases is the amount of tritium in the sample expressed as a ratio to a nominal concentration of 1 ^3H atom in 10^{18} H atoms.

Unlike stable isotope ratio measurements, which are effectively instantaneous, concentrations of ^{14}C and ^3H are often so low that counting of radioactive emissions may have to continue for a period of weeks to get a statistically meaningful result. In addition, tritium at low levels may require some pre-concentration (normally by electrolytic methods) before accurate measurements can be made. To some extent, problems formerly attending ^{14}C measurements have been overcome in recent years by the use of tandem accelerator mass

spectrometry (TAMS) which avoids the need for counting and can handle much smaller samples.

The two radioisotopes differ fundamentally both in terms of half-life and the way in which they have been incorporated into the water cycle. Firstly, radioisotopes are only useful for dating residences of up to six half-lives or so, because over longer intervals their emissions become too feeble to detect. Thus radiocarbon (half-life 5730 years) is limited to residence times of up to 30-40 ka, while tritium (half-life 12.4 years) is probably limited to no more than 100 years. Secondly, ^{14}C is continually being produced in the atmosphere and being incorporated into recharging groundwaters as part of their dissolved inorganic carbon (DIC) load, whereas nearly all the ^3H in groundwater is thought to be the result of recharge in the few years following the last major atmospheric thermonuclear tests in the 1960s.

However, despite the different half-lives and systematics of the two radioisotopes, the waters of most UNSAs are likely to be amenable to investigations using one or the other (and sometimes both) isotopes. A fuller discussion of both radioisotopes can be found in Fritz and Fontes (1980).

3. CASE STUDIES INVOLVING THE USE OF ISOTOPIC METHODS IN THE INVESTIGATION OF UNSAs

3.1 Introduction

The use of isotopic methods is now routine in hydrogeological investigations in general, and there is therefore a not inconsiderable body of data relating to UNSAs worldwide. The aim of this section is to consider in some detail the application of isotopic techniques to the various different representative environments identified by Mathers and Zalasiewicz (1993) in their guide to the sedimentology of UNSAs, using a selection of published case studies to illustrate particular points. Examples will be drawn from the developing world as far as possible.

3.2 Alluvial systems

The aim of this section is to cover deposits related to the action of rivers and streams, including alluvial fans but not deltaic systems, which will be considered in the next section.

Wet alluvial fans, though less common than dry alluvial fans, are found particularly in association with large upland regions such as the Himalayas. In Nepal, Siegel and Jenkins (1987) studied the fan of Tinau River system using ^{18}O , ^2H and ^3H . They found local, intermediate and regional scale groundwater flow systems, with estimated average groundwater velocities of $2\text{-}3\text{ md}^{-1}$, which compared favourably with velocities determined from pumping tests. Fig. 1 shows a cross section of the fan aquifer with tritium results and the inferred groundwater ages.

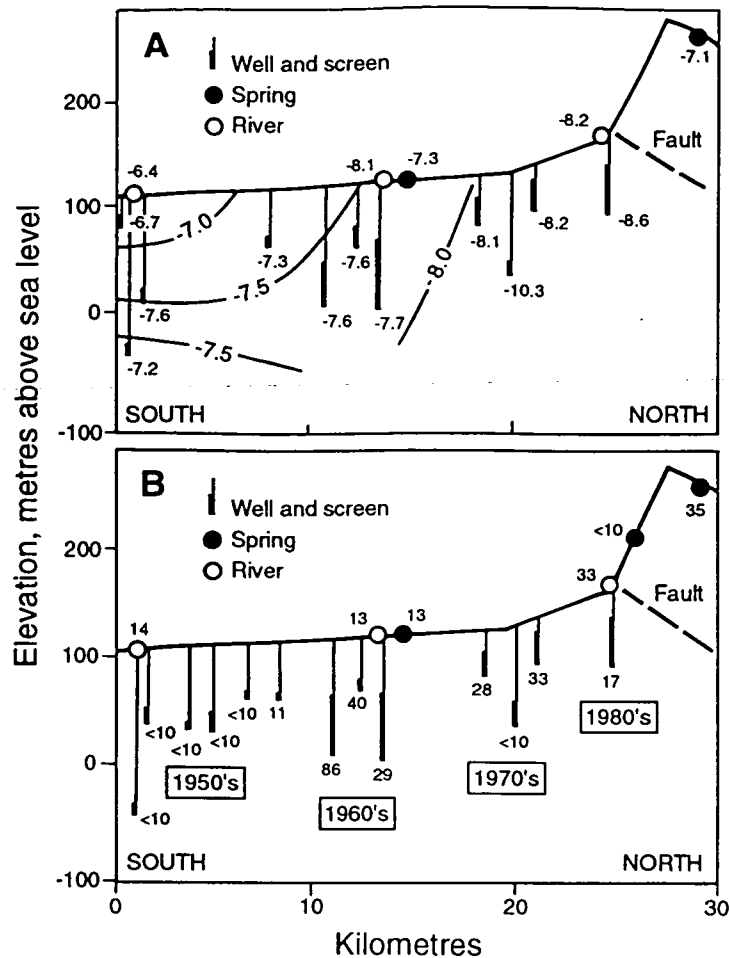


Fig. 1 Cross-section through alluvial fan aquifer in S Nepal, showing (a) $\delta^{18}\text{O}$ values in ‰, and (b) ^3H values in TR, plus inferred groundwater ages: (After Siegel and Jenkins, 1987.)

In Western Argentina, Albero *et al* (1987) investigated groundwater in the Tulum Valley. On the basis of ^{18}O , ^2H and tritium, they determined that groundwater is mainly recharged by the San Juan River which originates in the high Cordillera of the Andes. By contrast, rainfall over the valley itself contributed little to the groundwater inventory.

Dry alluvial fans and associated deposits in arid and semi-arid terrain have been more frequently studied using environmental isotopes. One of the earlier studies was carried out by Gonfiantini *et al* (1974) in the Hodna region of Algeria. A large number of measurements of ^{18}O , ^2H , tritium and radiocarbon made a very clear distinction between the origins of shallow and deep groundwaters (Fig. 2), and showed that the deeper water, which had been recharged under cooler climatic conditions, could not be contributing significantly to the water balance of the shallow alluvial aquifer, which was likely to be recharged by modern wadi flow. This lack of a hydraulic connection between alluvial and deeper regional aquifers has been confirmed elsewhere in northern Africa, e.g. by Darling *et al* (1987) in Sudan (Fig. 3).

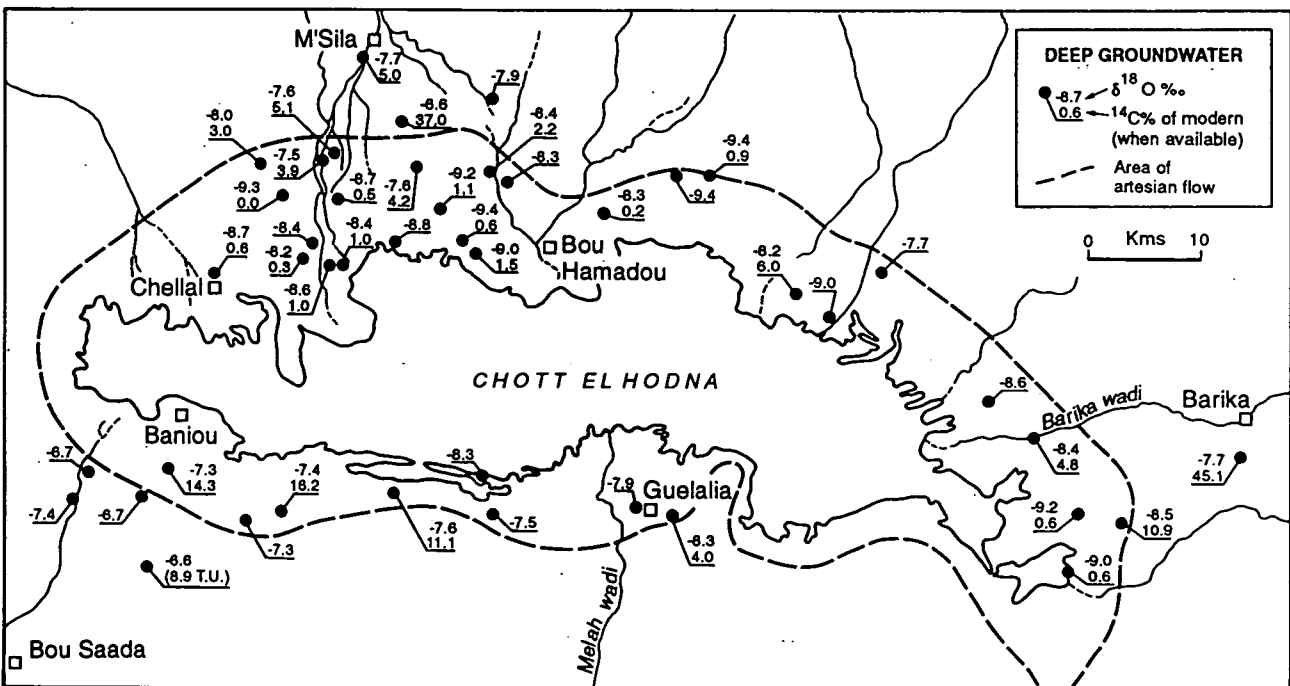
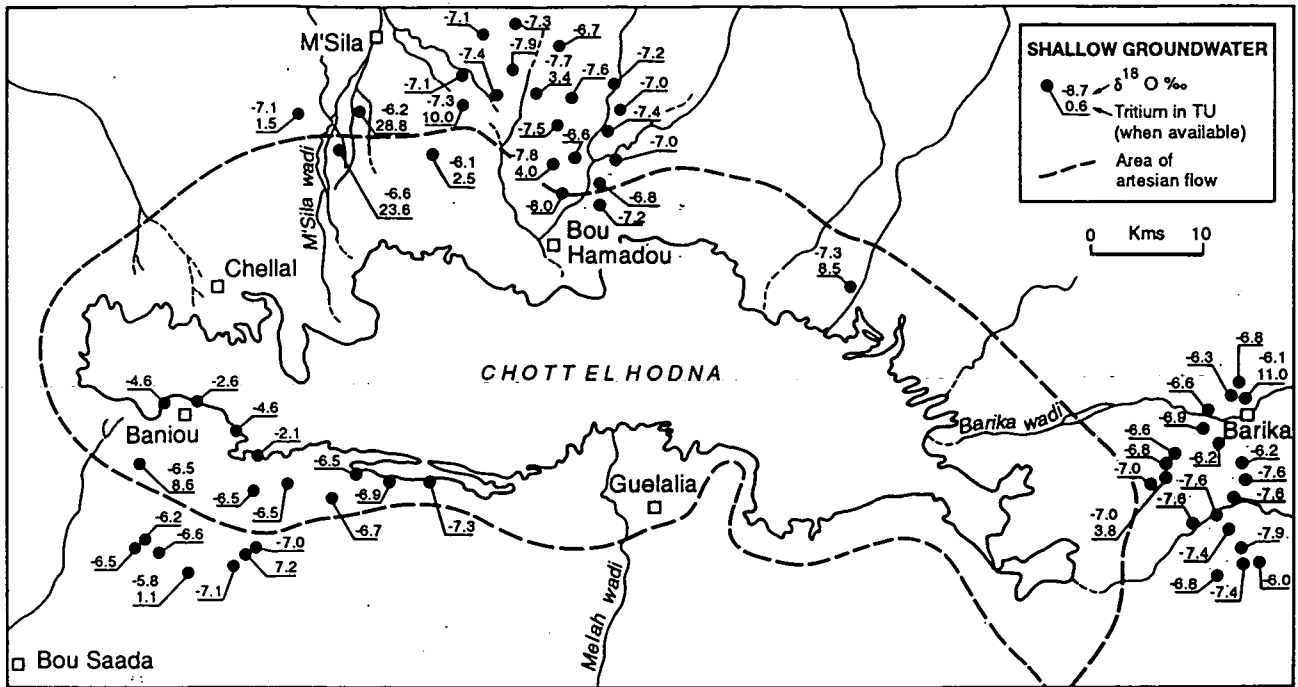


Fig. 2 Map of the Hodna region, Algeria showing $\delta^{18}\text{O}$ values in ‰ and ^3H values in TR for (a) shallow groundwaters and (b) deep groundwaters: The dotted line defines the area of artesian flow. Note that in general the deeper groundwaters have a more depleted ^{18}O composition and a lower ^3H activity, thus differentiating the source and age of recharge from the shallow groundwaters. (After Gonfiantini *et al*, 1974.)

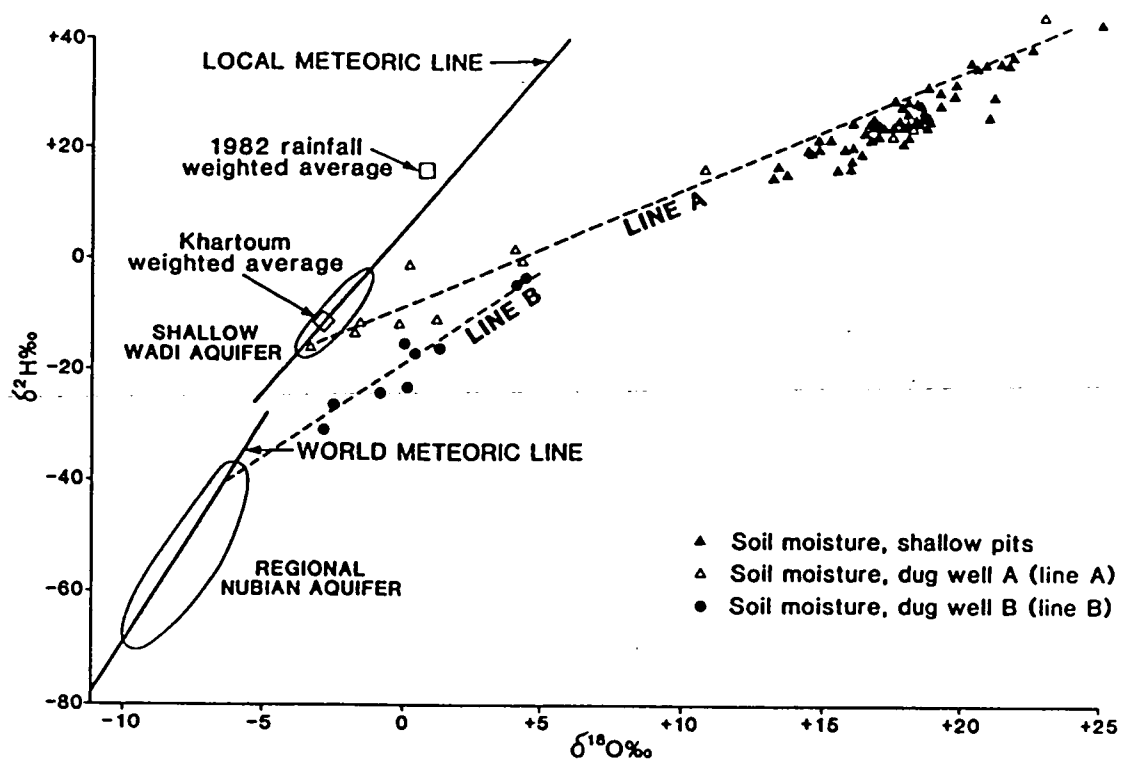


Fig. 3 Plot of $\delta^2\text{H}$ versus $\delta^{18}\text{O}$ for waters in the Abu Delaig area of NE Sudan. The composition of waters in the shallow wadi aquifers is similar to local rainfall but quite distinct from the regional aquifer underlying the area. Also shown are soil moisture profiles suggesting surface to aquifer diffusive gradients which differ according to the presence of absence of a shallow wadi aquifer (from Darling *et al*, 1987).

In the arid Northeastern Province of Kenya, Pearson and Swarzenki (1974) used radiocarbon and tritium measurements to investigate mechanisms of recharge to an aquifer in unconsolidated and semi-consolidated Tertiary and Quaternary sediments, underlying the Rivers Ewaso Ngiro and Lagh Dera. No detectable amounts of tritium were found, and ^{14}C values from 87.7 down to 2.8 pmc were measured which fell into several district groupings. On this basis, it was considered that the data indicated separate recharge events, at intervals of perhaps a few millennia, caused by extreme flood events. Much the same views were expressed by Sklash and Mwangi (1991) on the basis of O and H stable isotopic investigations in this and other parts of eastern Kenya.

Somewhat similar conclusions concerning episodic recharge to wadi aquifers in Djibouti were drawn by Fontes *et al* (1980), and Verhagen *et al* (1991), using ^{18}O , ^2H , tritium and radiocarbon. In this case, however, the often very low storage of groundwater in the volcanic rocks led to a range of groundwater 'ages' from old to recent. Despite this, there was evidence that there was little mixing in the subsurface between waters deriving from successive sporadic recharge events. Against this, exploitation of resources was causing radiocarbon pmc values to increase with time (Fig. 4), carrying the implication that an element of groundwater 'mining' was taking place.

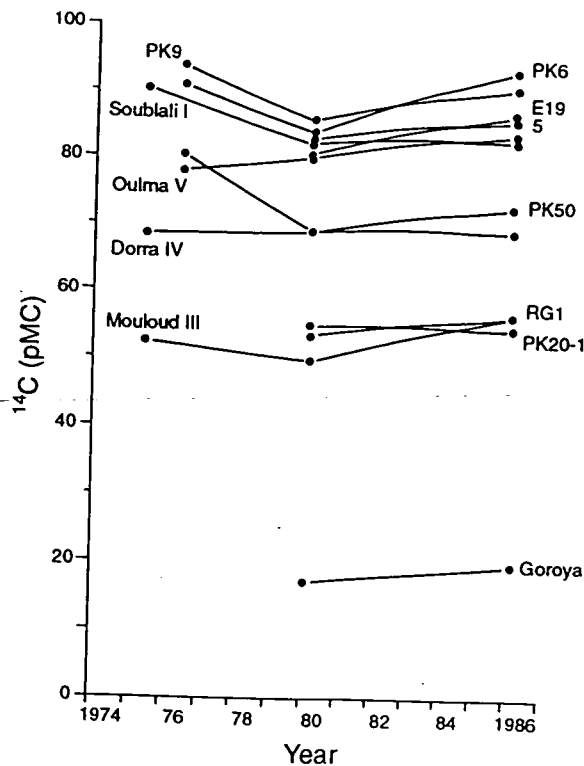


Fig. 4 Plot of ^{14}C against time for water supply wells in Djibouti. Note that in the 1980s, virtually all wells showed water decreasing in 'age' implying the gradual replacement of older, stored water by new reserves. (After Verhagen *et al*, 1991.)

Problems of waterlogging in the alluvial plains of the Mardan Valley, Pakistan, were investigated by Hussain *et al* (1992). Using ^{18}O and ^2H , they found that the source of waterlogging was usually leakage from irrigation canals, although in certain areas upward leakage from the deeper confined aquifer also contributed.

3.3 Deltaic deposits

The dividing line between alluvial and deltaic deposits is a fine one, but several isotopic studies of well-defined deltaic aquifers have been carried out.

The Okavango region of Botswana is a major wetland area occupying an inland delta. A comprehensive study by Dincer *et al* (1979) found that O and H stable isotopes could be of great assistance in water balance studies and groundwater relations. Fig. 5 shows a map of the delta, of which the swamp area alone occupies up to 13000 km², while Fig. 6 shows the $\delta^{18}\text{O}$ value of many ground and surface waters from the region. The rising $\delta^{18}\text{O}$ values are indicative of increasing evaporation. This can be more rigorously defined by plotting values on a set of theoretical $\delta^{18}\text{O}$ -EC curves (Fig. 7). These show how E/ET ratios vary for individual points with the seasons. These ratios are important because it is necessary for hydrological purposes to determine whether salinity and isotope variations result from evaporation (fractionating) or transpiration (non-fractionating) processes. These results could then be fed into a water-balance model.

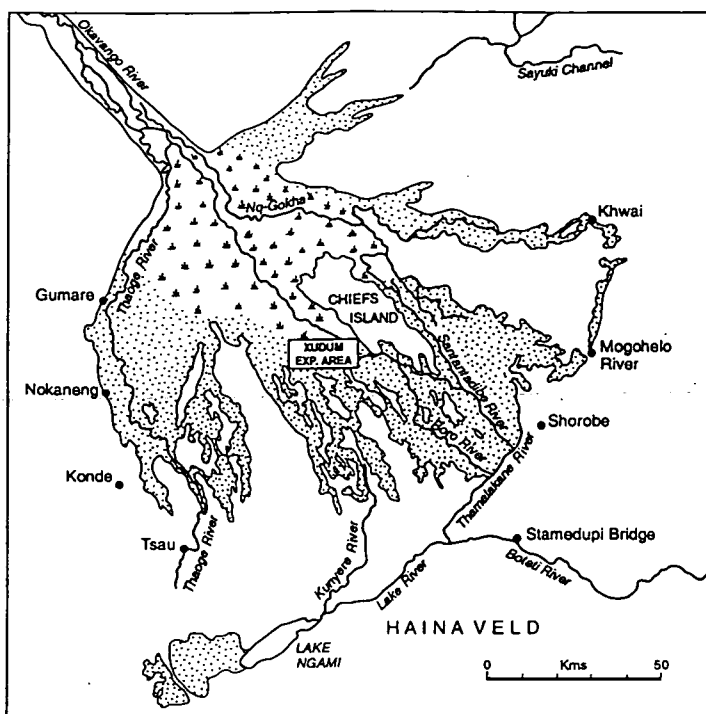


Fig. 5 Map of the Okavango Delta (Botswana), showing the location of sampling sites. (After Dincer *et al*, 1979.)

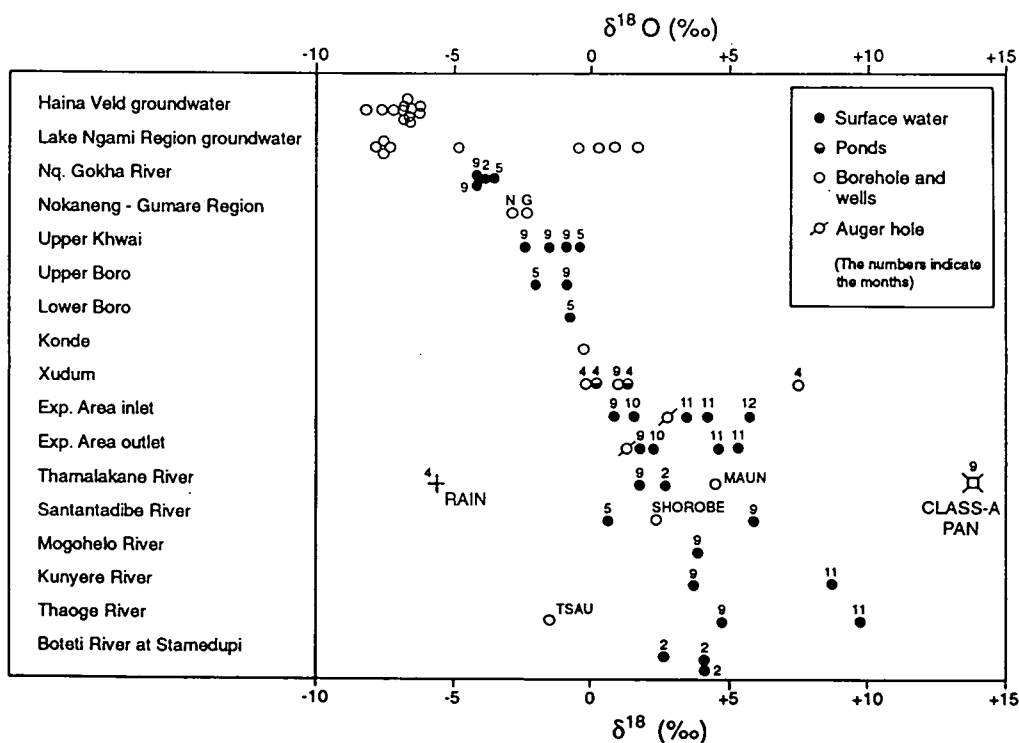


Fig. 6 Classification of Okavango Delta waters with respect to $\delta^{18}\text{O}$. (After Dincer *et al*, 1979.)

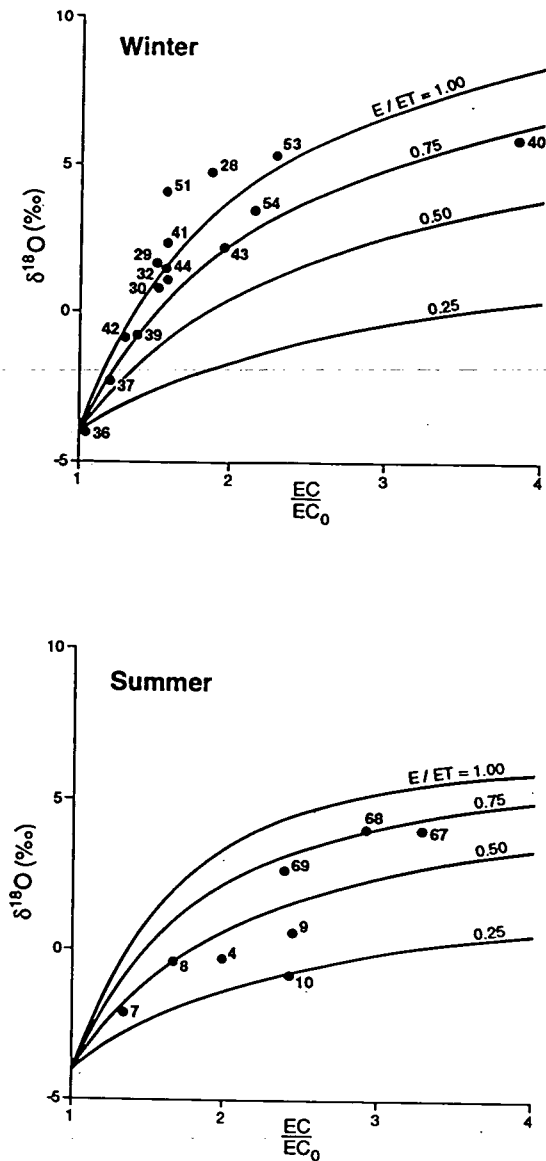


Fig. 7 Theoretical $\delta^{18}\text{O}$ electrical conductivity (EC) curves for different ratios of evaporation to evapotranspiration (E/ET) for (a) winter, (b) summer in the Okavango Delta. The E/ET ratios for the plotted points (location Fig. 5) can be interpolated. (After Dincer *et al.*, 1979.)

The Nile delta is also situated in a semi-arid area, but in this case adjacent to the sea. As part of the investigations of Geirnaert and Laeven (1992), environmental isotopes were employed in the role of tracers (^{18}O , ^2H) and as residence indicators (^3H , ^{14}C). The stable isotopes in conjunction with chloride data were used to define sources of salinity, mainly evaporation rather than mixing with marine waters in this case. The radioisotopes allowed a recharge history going back to the late Pleistocene to be developed, and at the same time permitted the classification of groundwaters into recent, sub-recent and fossil types, thus carrying important implications for groundwater extraction.

Another coastal delta, but in a humid environment, is the Mekong Delta of Vietnam. This delta is a complex series of sediments with several aquifers (Holocene, Pleistocene, Pliocene) overlying a basement aquifer. In addition to the Mekong River, the Bassac River is also an important source of recharge. Tidal intrusions of up to 100 km inland have left surface waters saline, leading to great dependence on groundwater and potential for overexploitation leading to salinisation and subsidence.

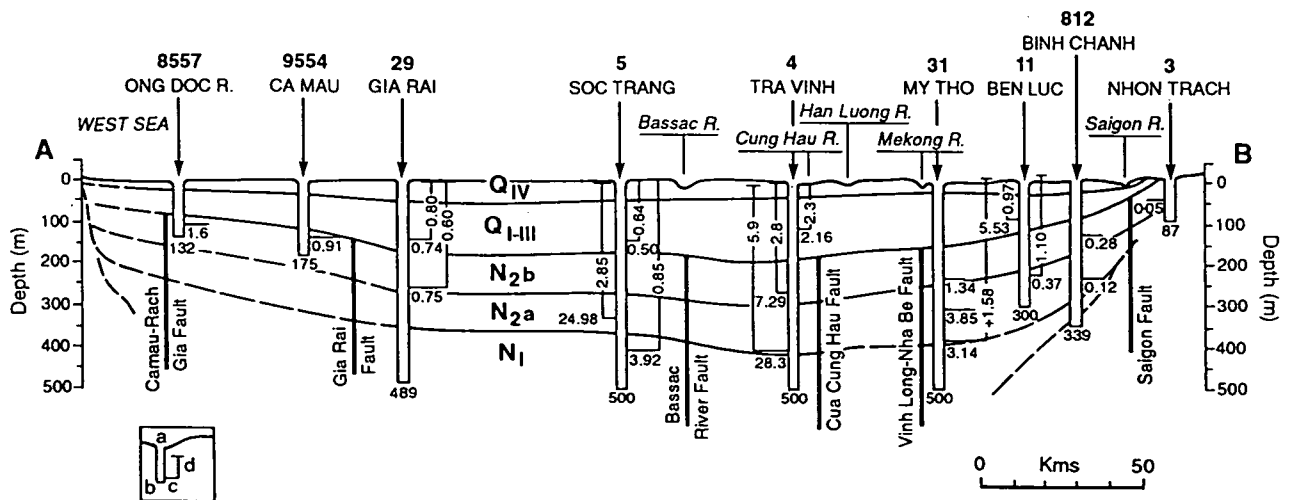
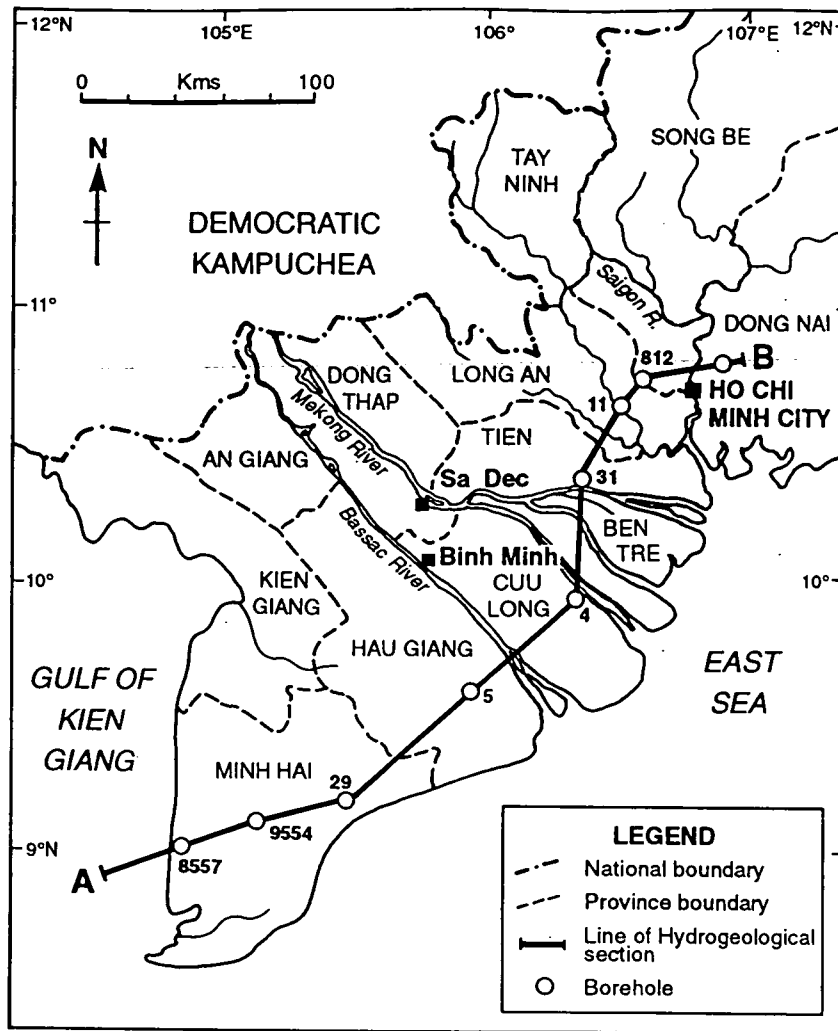
The most recent aquifer (Holocene) covers most of the delta and is up to 55 m thick at the centre. The heterogeneous sediments have a generally low permeability, while in some places sandy lenses give rise to conditions of semi-confinement. The Pleistocene aquifer occurs mainly in the north and northeast, and is confined where covered by the Holocene. The Upper Pliocene aquifer also occurs in the north and northeast. It is mainly confined in the delta, and in the crustal zone of the northeast becomes saline. Fig. 8 shows a map of the delta, and Fig. 9 a SW-NE cross section showing the various aquifer units (Ho *et al*, 1992). (The aquifers of the Lower Pliocene and basement are not regarded as UNSAs for the purposes of this review.)

Stable isotope data show that the Holocene aquifer waters contained modern water, sometimes having suffered evaporation. In the Pleistocene aquifer, there is evidence for a rise in chloride due to dissolution processes (Fig. 10a), whereas the underlying upper Pliocene aquifer shows that mixing with seawater is an important source of salinity (Fig. 10b).

Radiocarbon data allow estimations of groundwater transit times, but only in the confined aquifers. Ho *et al* (1992) modelled radiocarbon 'ages' for sample sites across the delta, and arrived at groundwater ages of up to 35 ka (Fig. 11) in the Pleistocene aquifer, implying an average flow velocity of 5.7 ma^{-1} . In the Upper Pliocene aquifer flowpaths are more complicated, but an average flow velocity of around 2.5 ma^{-1} was estimated for most of the aquifer.

Fig. 8 (Opposite, upper) Map of the Mekong Delta, Vietnam. The cross-section defined by line B-B is depicted in Fig. 9. (After Ho *et al*, 1992.)

Fig. 9 (Opposite, lower) Cross-section through the aquifer units of the Mekong Delta. Q_{IV} - Holocene; Q_{I-III} - Pleistocene; N_2^b Upper Pliocene; N_2^a Lower Pliocene; N_1 - Miocene; M_2 - Mesozoic; a - borehole number; b - depth of borehole; c - TDS in gl^{-1} ; d - piezometric level in m. (After Ho *et al*, 1992.)



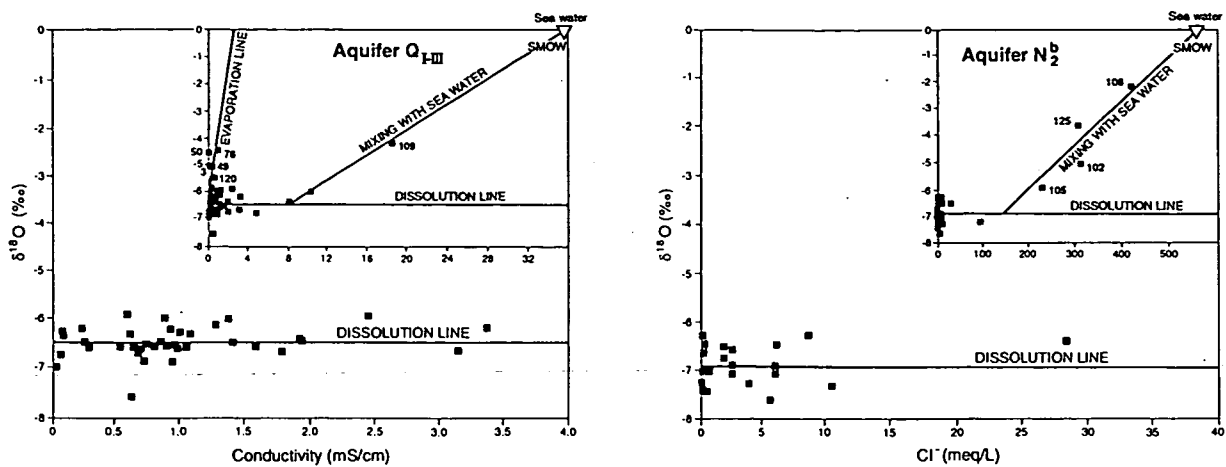


Fig. 10 Plots of $\delta^{18}\text{O}$ in ‰ versus conductivity in mS cm^{-1} for (a) the Pleistocene, and (b) the Pliocene aquifers of the Mekong Delta. Note the influence of halite dissolution in (a), but seawater mixing in (b) as causes of increasing salinity. (After Ho *et al*, 1992.)

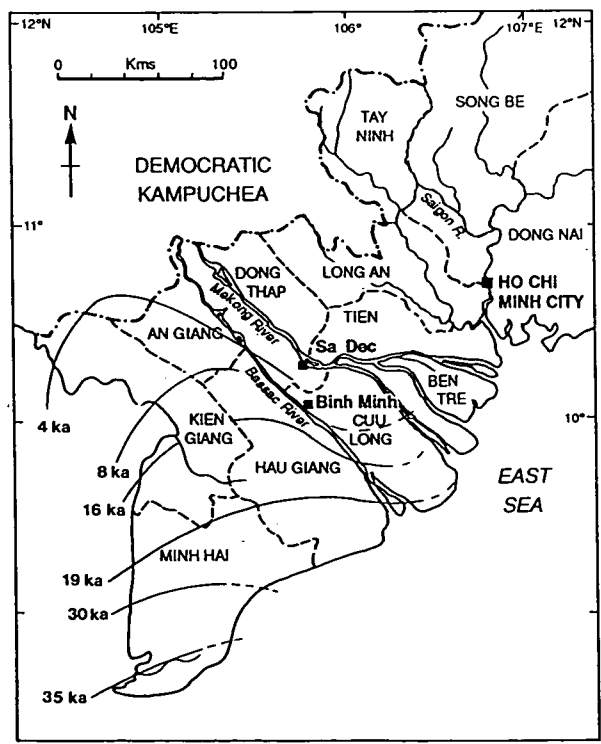


Fig. 11 Distribution of ^{14}C isochrones for the Pleistocene aquifer of the Mekong Delta. (After Ho *et al*, 1992).

3.4 Coastal deposits

In groundwaters within coastal sediments, environmental isotopes are used in ways similar to those employed for the investigation of deltaic groundwater bodies: i.e. to identify sources of salinity and possible relationships between aquifers.

Yurtsever and Payne (1979) studied groundwaters in the Qatar peninsula. Here, aeolian and alluvial deposits are often above the water table, but in some areas contain a water resource. Stable isotopes were able to distinguish between areas where increasing salinity was due to seawater intrusion, and where it was caused by leakage from underlying saline 'formation' waters.

The Cul-de-Sac plain of Haiti was investigated using environmental isotopes by Gonfiantini and Simonot (1987). They found two areas where saline groundwaters were present: the northern belt of the plain (where low-permeability marine clays predominate, in contrast to the thick alluvial deposits of the rest of the plain), and in the coastal area to the north and east of Port-au-Prince (Fig. 12). Although stable isotopes indicated that seawater was likely to be the source of salinity for both categories (Fig. 13), radiocarbon ages of > 10 ka were shown by two of the most saline wells of the northern belt, implying that residual seawater was responsible, rather than the modern seawater intrusion caused by over-exploitation of groundwater in the coastal parts of the Port-au-Prince region.

A comprehensive hydrogeochemical study of the Midnapore coastal plain of West Bengal (Fig. 14) was carried out by Shivanna *et al* (1993), using environmental isotope techniques with a view to establishing sources of salinity, estimating residence times and investigating recharge of potable waters. The coastal plain is covered by poorly consolidated alluvial deposits, including clays, sands and gravels, which because of marine transgression and regression in the late Pleistocene and early Holocene are interlayered in an irregular fashion.

Plots of $\delta^2\text{H}$ and Cl versus $\delta^{18}\text{O}$ (Fig. 15) show evidence of seawater mixing for a majority of samples, though heavy isotope enrichments in the North Midnapore area are more likely to be evaporative in origin. Radioisotope information showed residence times up to around 9 ka, showing that some parts of the groundwater body have been in isolation since the period of the Flandrian transgression and that the source of salinity is likely to be seawater of this age.

3.5 Volcanic deposits

Volcanic rocks vary from massive lavas through friable tuffs to cinder beds in degree of consolidation, resulting in a whole range of hydrogeological environments, often found in close and chaotic proximity to each other. The study of groundwater movements in volcanic terrains therefore rarely involves unconsolidated sediments only. Nevertheless, there are cases where isotopic methods have been applied to investigations which have some relevance to UNSAs.

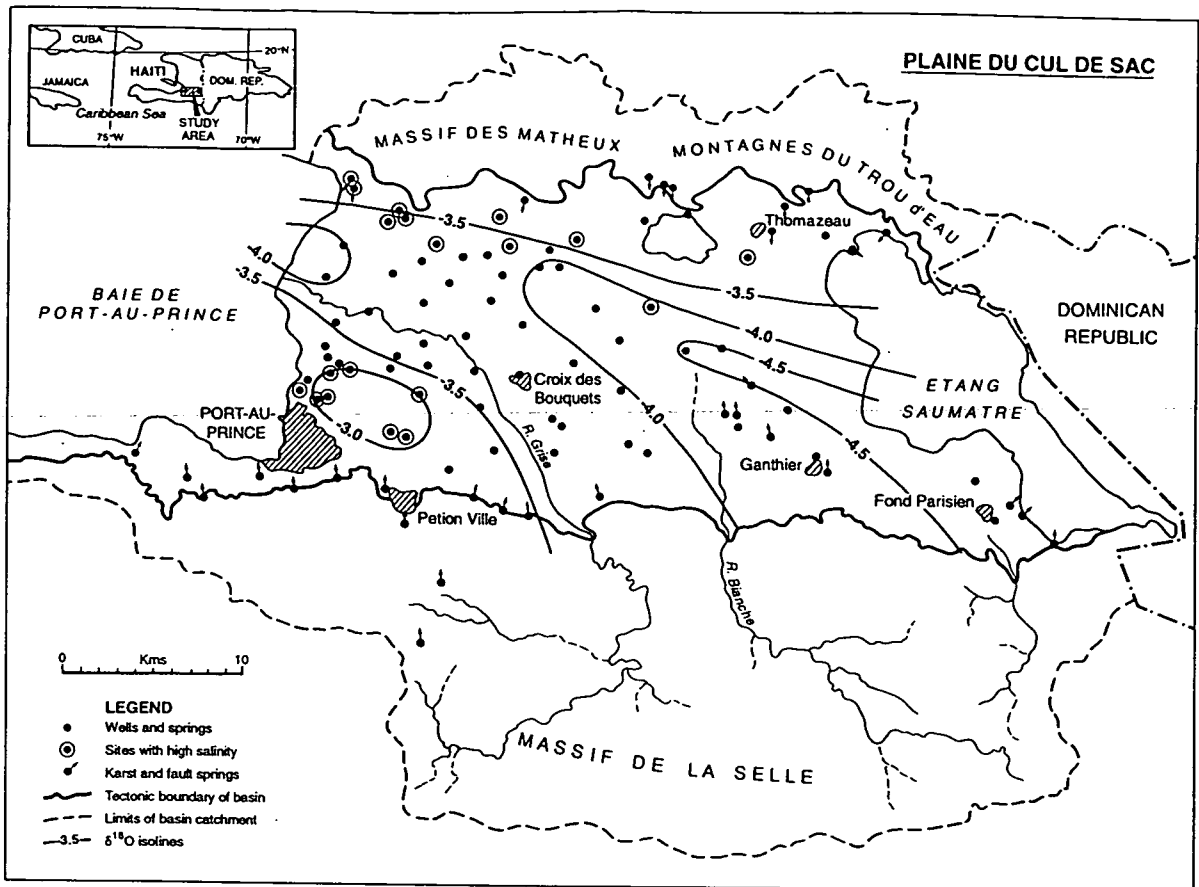


Fig. 12 Geographical distribution of $\delta^{18}O$ values in groundwaters of the Cul-de-Sac Plain, Haiti. Circlets denote sites with high salinity (EC above $1500 \mu\text{Scm}^{-1}$). δ -value isolines indicate the origin and main flow patterns of groundwater. (After Gonfiantini and Simonot, 1987.)

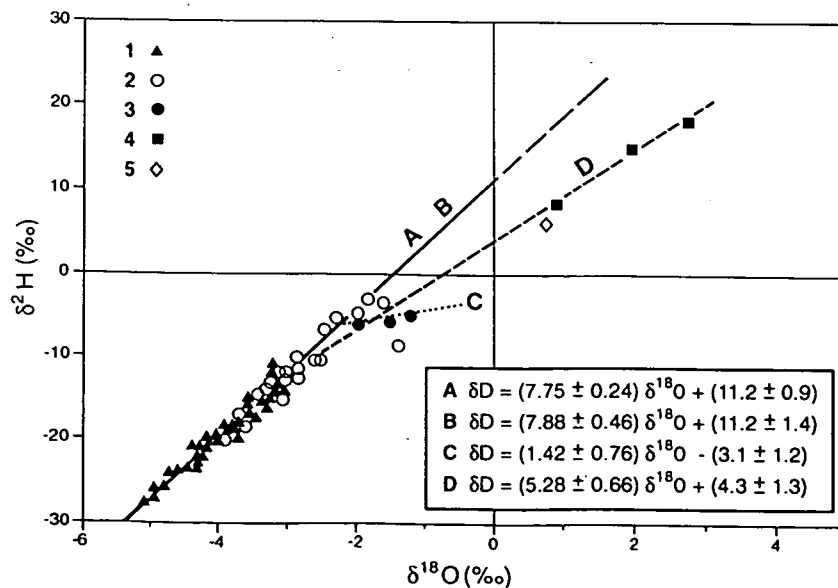


Fig. 13 Plot of $\delta^{2}H$ versus $\delta^{18}O$ for groundwaters in the Cul-de-Sac plain. 1, A - karst springs, diffuse springs and freshwater wells; 2, B - saline wells; 3, C - fault springs; 4, D - lakewaters; 5 - sea. (After Gonfiantini and Simonot, 1987.)

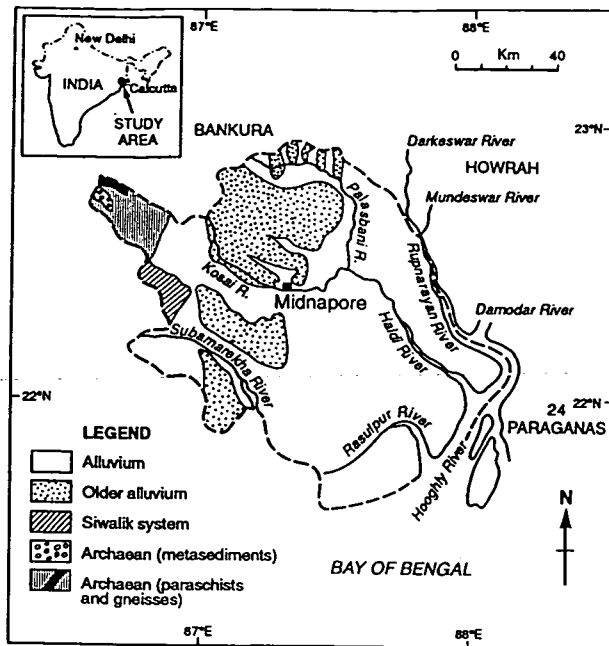


Fig. 14 Map of the Midnapore coastal plain, West Bengal. (After Shivanna *et al*, 1993).

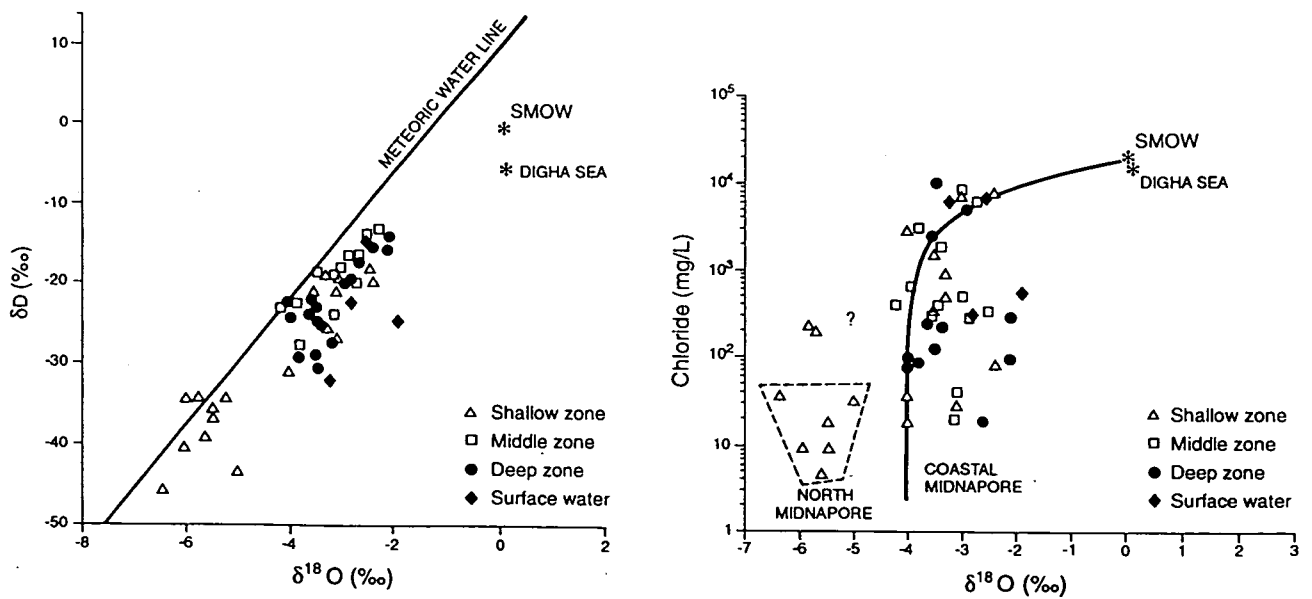


Fig. 15 Plots of (a) $\delta^2\text{H}$, and (b) Cl versus $\delta^{18}\text{O}$ for Midnapore groundwaters. (After Shivanna *et al*, 1993).

For example, in central Mexico the hydrogeology of the Trans-Mexican Volcanic Belt (TMVB, Fig. 16) was investigated by Issar *et al* (1984). Using the deuterium-excess or 'd' parameter (which is basically an index of deviation from the world meteoric line), these authors arrived at a hydrological/hydrochemical flow chart (Fig. 17), which summarises the water cycle in the TMVB.

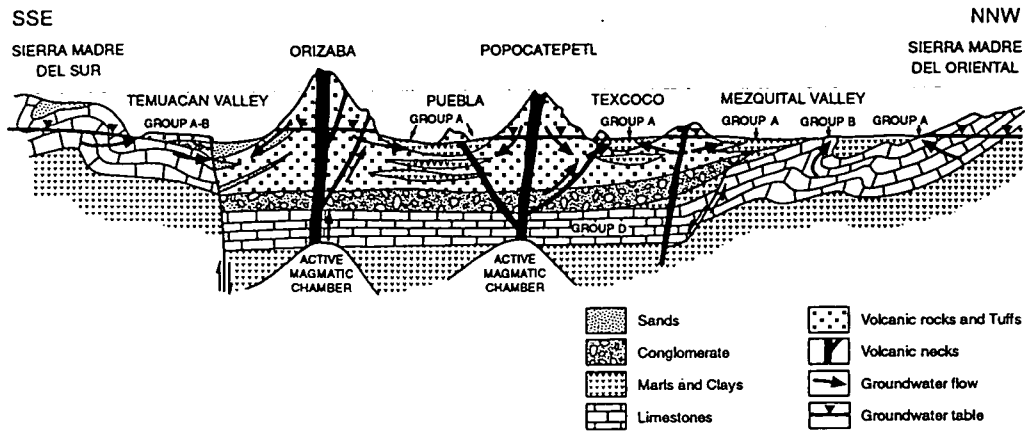


Fig. 16 Geological cross section through the Trans-Mexican Volcanic Belt, showing directions of groundwater flow in the various aquifer units. (After Issar *et al*, 1984).

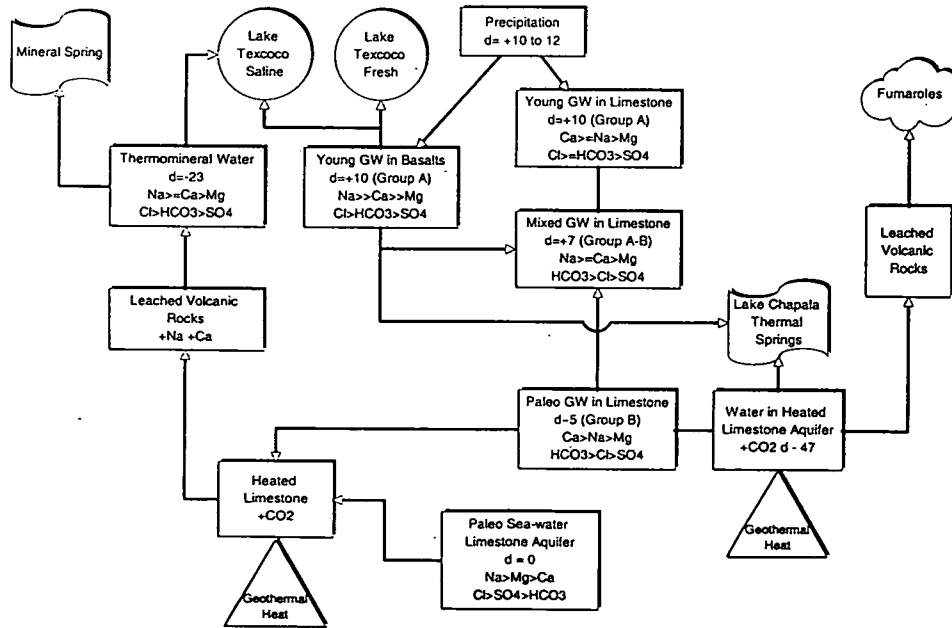


Fig. 17 Hydrological and hydrochemical flow chart for the Trans-Mexican Volcanic Belt, showing the use of 'd' (deuterium excess) values in conjunction with water chemistry in tracing the complex interactions and flowpaths between the various volcanic and sedimentary aquifer units (GW-groundwater). (After Issar *et al*, 1984.)

Further south, in Costa Rica, the isotope hydrology of the volcanic aquifers was studied by Darling *et al* (1987) using ^{18}O , ^2H and ^3H . Fig. 18 shows a typical cross-section through the aquifer units. This reveals that most flow occurs through lava breccias. Interestingly, highest tritium concentrations were measured in the middle aquifer, the Colima Superior. Also, stable isotopic depletions indicated enrichment in stable isotopes from the top down (Fig. 19). Normally, in terrain with high relief, lower aquifers derive their recharge from higher altitudes than upper aquifers, and consequently isotopic depletion is expected to occur with depth. Darling *et al* (1989) attributed the inverse relationship to a combination of the complicated climatic patterns of the region, whereby Pacific and Caribbean weather systems dominate at different times of year, and complicated geometry of the aquifers in the recharge area.

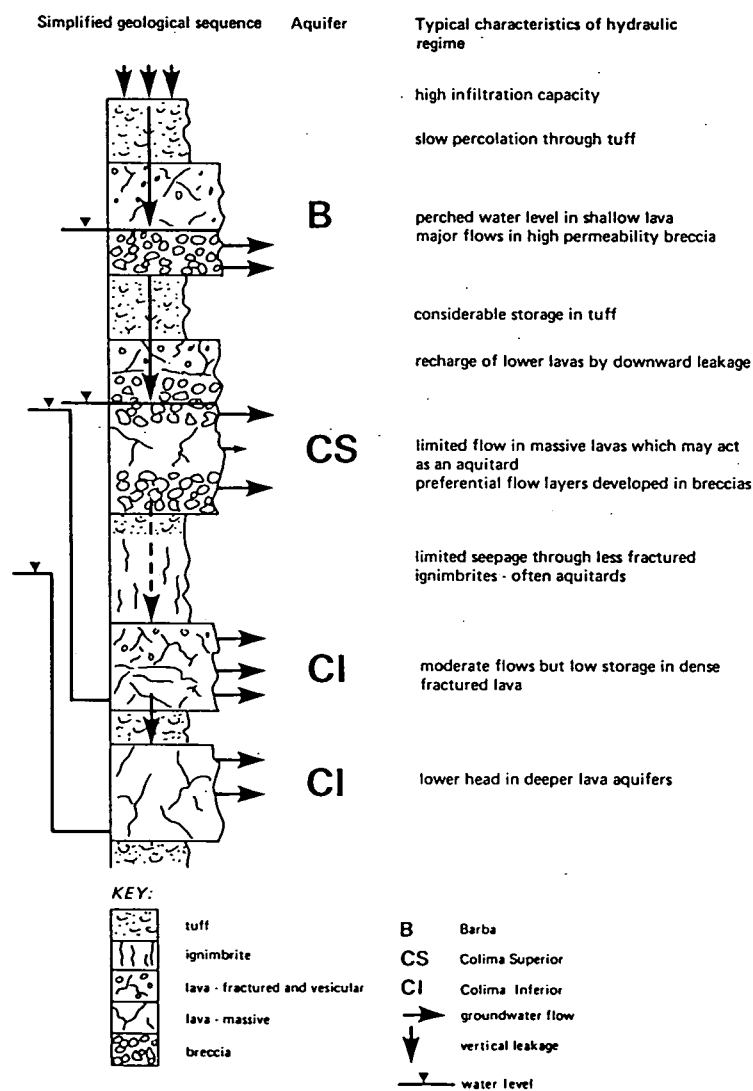


Fig. 18 Schematic vertical section through the Valle Central, Costa Rica volcanic aquifer system showing simplified geological sequence and groundwater piezometric levels. (From Darling *et al*, 1989.)

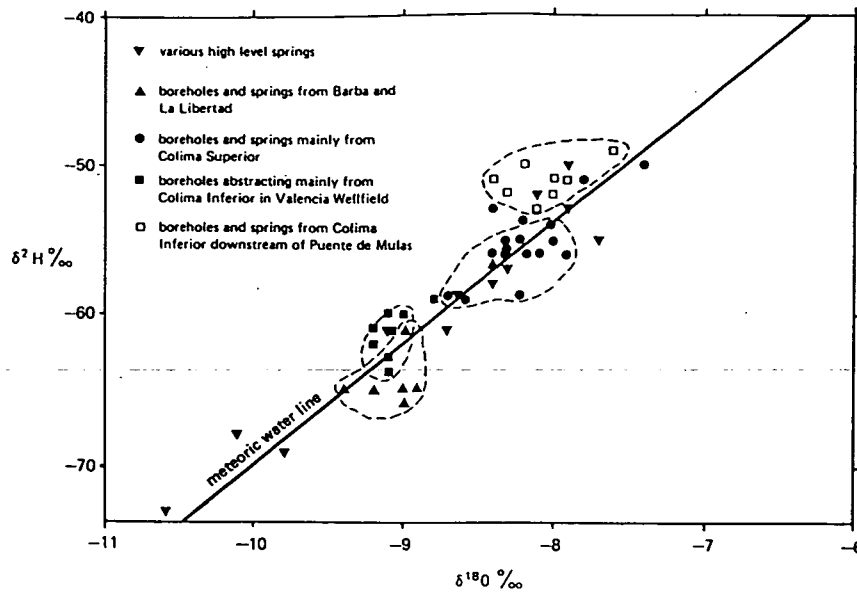


Fig. 19 Plot of $\delta^{18}\text{H}$ versus $\delta^{18}\text{O}$ for groundwaters from the various aquifer units in the Valle Central. Note that there is relatively little overlap between the various categories, which in this context suggests different altitudes of recharge. (From Darling *et al*, 1989.)

Volcanic aquifers on Gran Canaria (Canary Islands) were investigated by Gasparini *et al* (1990) primarily on the basis of environmental isotopes. They found that on this rugged island, relationships between increasing altitude and isotopic depletion depended on geographical position (Fig. 20). Once calibrated, these could be used to estimate the altitude of recharge for various groundwaters. In parts of the island free from the influence of volcanic CO_2 , principally in the Amurga area, waters with modelled radiocarbon ages of up to 11 ka were found. Elsewhere, despite the input of this 'dead' CO_2 into the carbonate system, higher amounts of ^{14}C were measured, implying significantly younger waters in the other areas.

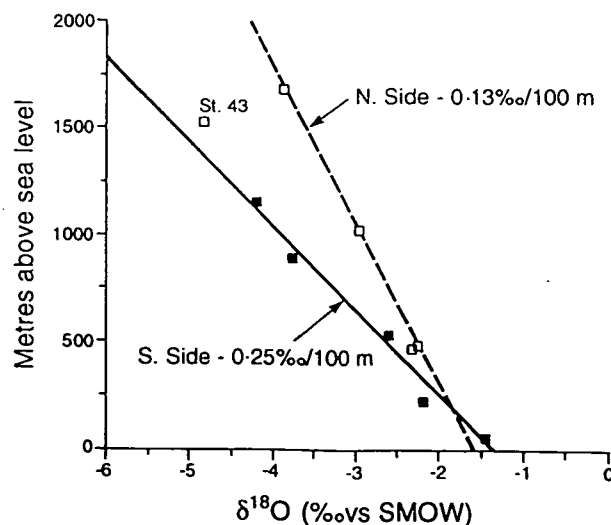


Fig. 20 Plot of $\delta^{18}\text{O}$ depletion with altitude for the northern and southern slopes of Gran Canaria (Canary Islands). (After Gasparini *et al*, 1990).

3.6 Glacial deposits

Rather little can be said specifically about the isotope hydrology of unconsolidated glacial sediments, which in any case are not particularly well-represented in developing countries, situated as many of them are in lower latitudes. Glacial deposits tend to divide into the highly permeable (sands, gravels) or poorly permeable (till or boulder clay). In isotopic terms the former are to all intents and purposes identical to alluvial sands and gravels, while the latter are often considered to be aquitards.

Isotopic studies of glacial deposits fall into two types: those which are concerned with deposits resulting from past glacial activity, and those with catchments where glacial meltwater still plays an important tracer role. In the former category, Andersen and Sevel (1974) studied unsaturated zone cores from fluvio-glacial outwash deposits in Denmark. Their studies, using tritium, were largely concerned with the quantification of recharge rate through the sands and gravels. By contrast, Desaulniers *et al* (1980) concentrated on a much more impermeable sequence of clayey till and glaciolacustrine clays in southwest Ontario. Using ^{18}O , ^2H and ^{14}C in addition to ^3H , they established that porewaters in these clays are a diffusive mixture of late Pleistocene and modern groundwaters.

In the latter category, a typical use of isotopic methods has been to separate hydrographs. At the large scale, Prantl and Loijens (1977) measured tritium concentrations in creek, river, firn and ice samples in the drainage basin of the North Saskatchewan River for a period of three years in order to quantify the contributions of various parts of the water cycle. For example, in the month of July they estimated the discharge of the main river to consist of 10% snow melt, 20% ice meltwater, and 70% subsurface storage water. On a smaller scale, Dincer *et al* (1970) and Martinec *et al* (1974) used tritium to estimate basin residence times in two Central European catchments, and from these to calculate subsurface volumes of $2.6 \times 10^6 \text{ m}^3$ and $130 \times 10^6 \text{ m}^3$ respectively. At the stream scale, Rodhe (1984) investigated the hydrology of forested till soils using $\delta^{18}\text{O}$. He determined that even during spring-melt floods, an average of 85% of the discharging water came from subsurface storage.

3.7 Lacustrine deposits

Just as many (though by no means all) glacial deposits have an alluvial equivalent, so lakes too may have deposits analogous to those laid down by rivers, all of which may have very similar hydrological characteristics. In 'active' glacial systems the isotopically depleted nature of meltwater inputs can easily be separated from ambient waters further downstream. Similarly, the isotopically enriched waters often found in lakes owing to evaporative processes provide an equally distinctive compositions in cases where lakes may be recharging groundwater.

In most cases, studies have shown that recharge from lakes to the surrounding sediments tends to be local in scale. For example, this was observed for the dune sediments to the east of Lake Chad in central North Africa by Fontes *et al* (1970), who explained the rather complex hydrogeochemistry of the local aquifer in terms of the schematic of Fig. 21. Note that in this case the level of the lake (which is fed by rivers some distance away) is at its highest in the local dry season. Lake-derived recharge to local sediments was also noted by Darling *et al* (1990) using O and H isotopes. Fig.22 shows the area around Lake Naivasha in Kenya, with contours showing the percentage of lakewater in the lakewater-meteoric groundwater mixing continuum. These authors also used a unique isotopic technique - stable isotope ratios in fumarolic steam - to show that water flows at least 30 km from the lake in volcanic and volcanoclastic aquifers.

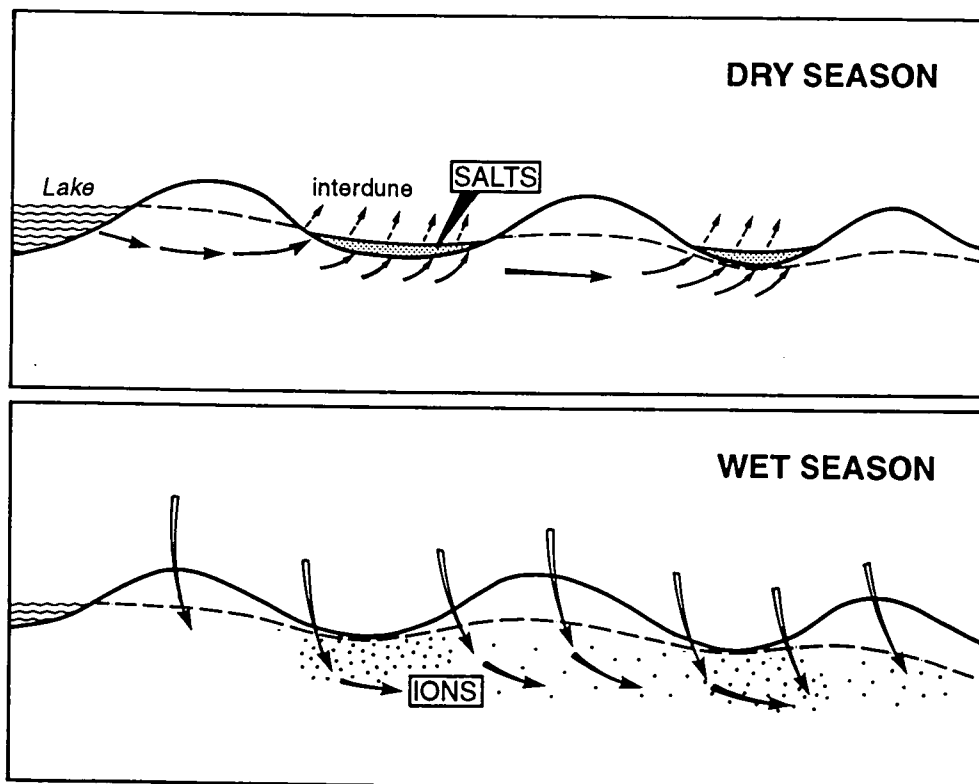


Fig. 21 Schematic diagram to explain water levels and hydrochemistry of the dune aquifers lying to the east of Lake Chad (central North Africa). (After Fontes, 1980.)

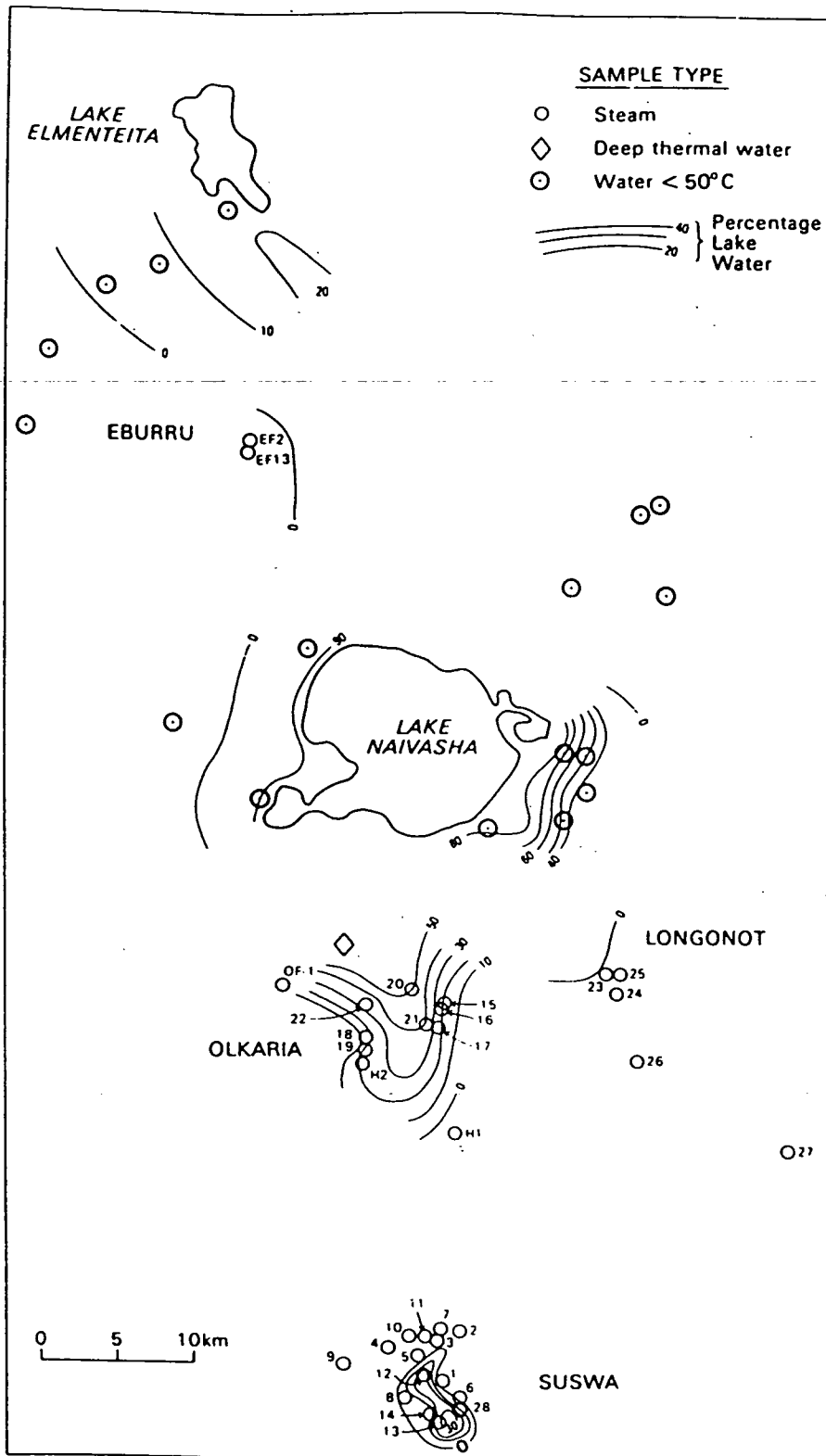


Fig. 22 Contour map of percentage of lakewater in the groundwater system of the Lake Naivasha region, Kenya Rift Valley. Note that the contours near the lake and to the north are mainly defined on the basis of well water analyses, while those to the south have been determined (with suitable correction) from analyses of geothermal steam. (From Darling *et al*, 1990.)

3.8 Aeolian deposits

By their very nature, aeolian deposits tend to occur in dry areas such as deserts where they generally form a mantle overlying more consolidated rocks. Except for areas where this mantle is very thick, aeolian deposits generally only become aquifers locally, for example when a river gives rise to recharge by leakage. Thus interest in aeolian deposits is frequently connected with their 'unsaturated zone' role. The case studies considered below are restricted to blown sands; although loess may give rise to very thick deposits in dry temperate regions (e.g. the North China Plain), it seldom possesses good aquifer properties.

The Gordonia region of South Africa abuts the border with Botswana and can be regarded as part of the Kalahari Desert. There is an almost unbroken cover of parallel sand dunes which are fixed under current climatic conditions by vegetation. The underlying rocks consist of the unconsolidated Kalahari Beds and shales and tillites of the Karoo. Mostly groundwater is restricted to the Karoo and lower Kalahari Beds, but in the vicinity of rivers recharge to the local sands may occur (Verhagen, 1984).

The O and H stable isotopic content of various groundwaters is shown in Fig. 23. It is apparent from this crossplot that there is little overlap between the compositional ranges of the river aquifer waters and the deeper 'Kalahari trough' and 'other groundwaters' categories which make up the bulk of groundwaters. This implies that these categories are not related to river recharge, but arise from direct infiltration through the dune sands of more local, less depleted meteoric waters which are often affected by evaporative fractimation in the soil zone, thus causing them to deviate from the meteoric line. The saline waters show pronounced effects of evaporative enrichment and have probably resulted from ponding in shallow pans before infiltration.

Though not in any sense a developing country, Australia has arid and semi-arid areas, the water balance of which in some areas has been studied in considerable detail. One area to the east of the River Murray, where sand dunes overlie calcretes, was investigated by Allison *et al* (1985). Here, late Pleistocene and early Holocene dunes have accumulated under the influence of westerly winds. Fig. 24 shows a cross-section through the area investigated, while Fig. 25 shows the water content, chloride content and stable isotope compositions for two boreholes in the cleared dune part of the section. Taken in conjunction with the local groundwater isotope values, which are similar to the quasi-steady state compositions towards the bottom of the profiles, it appears that active recharge is taking place. This can be approximately quantified by chloride balance techniques to show that the long term average recharge rate is 14 mma^{-1} , and that the high Cl concentrations stored within the dune sand will be a source of groundwater salinity for many thousands of years.

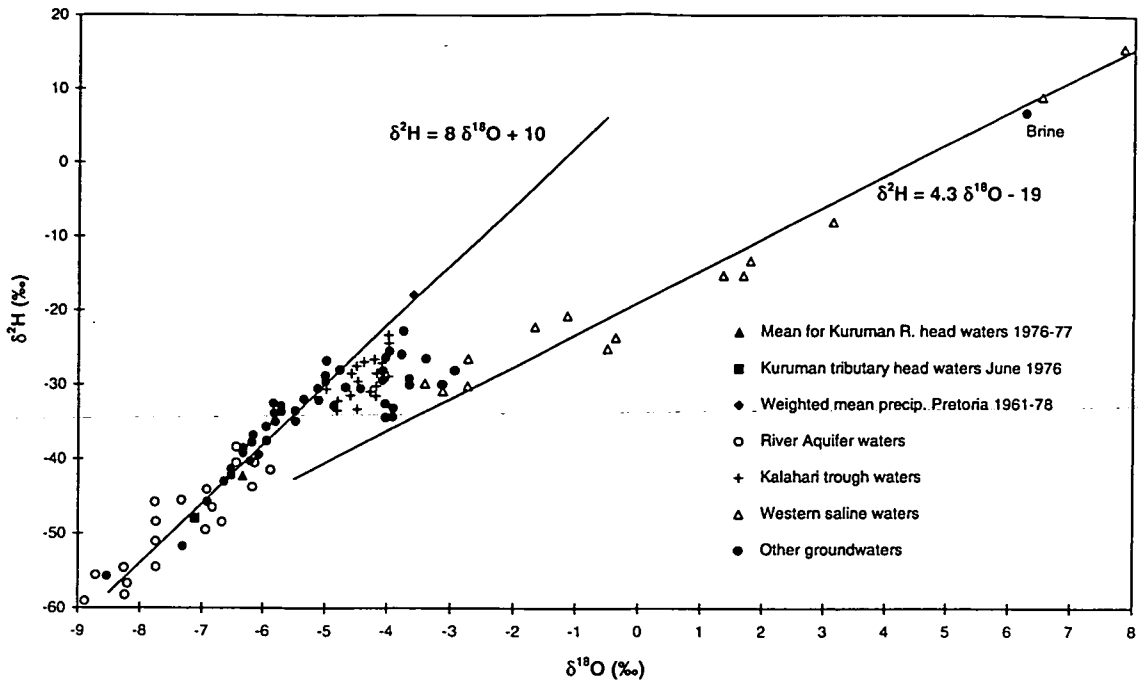


Fig. 23 Plot of $\delta^2\text{H}$ versus $\delta^{18}\text{O}$ for aquifers in the Gordonia area of the South African Kalahari. Note that the waters of the dune aquifers recharged by river water are more depleted than the 'Kalahari trough' and 'other' groundwaters away from the river, indicating that those more distant groundwater receive direct recharge from rainfall. Saline water results from evaporation from salt pans. (After Verhagen, 1984.)

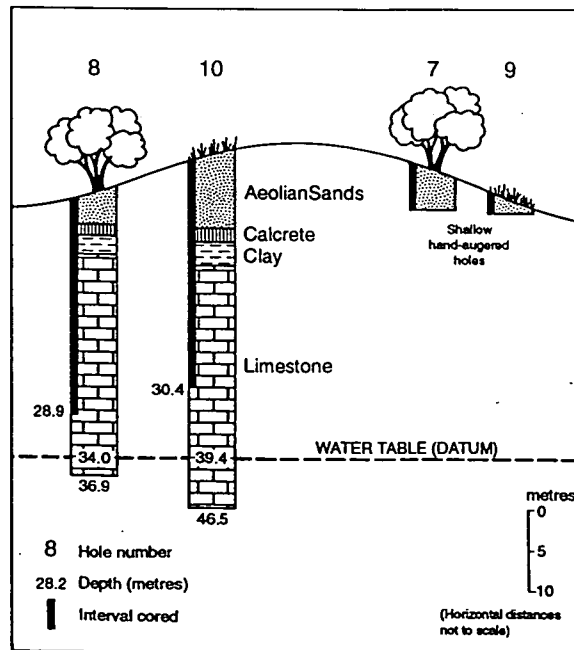


Fig. 24 Schematic cross-section through a partly dune-covered site of South Australia, showing the disposition of various auger holes. (After Allison *et al*, 1985.)

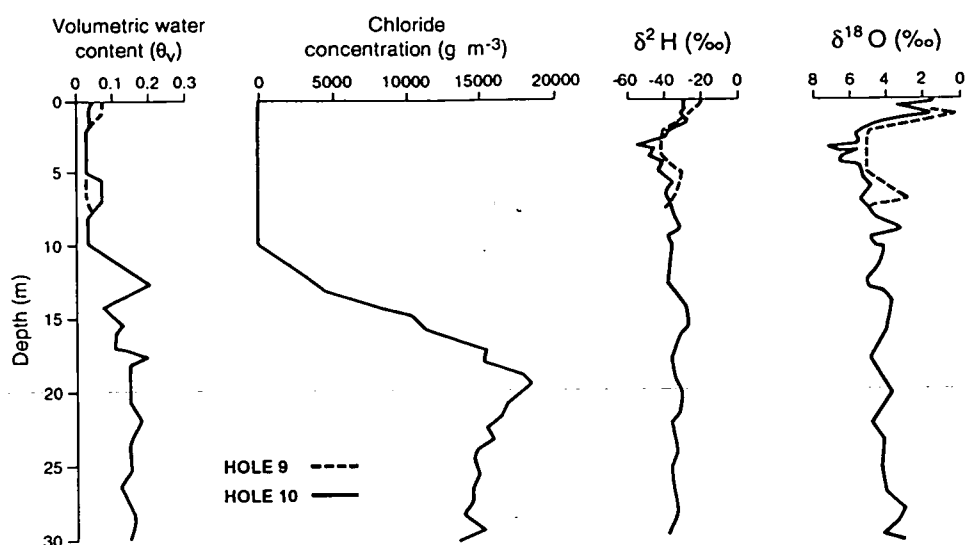


Fig. 25 Water content, chloride content and isotope composition for porewaters from auger holes drilled on a cleared dune area, South Australia (refer to Fig. 24 for hole details). Values of $\delta^2\text{H}$ and $\delta^{18}\text{O}$ below 10-15 mbgl are similar to groundwater compositions in the area, but note the large amount of chloride stored in the profile. (After Allison *et al*, 1985).

4. CONCLUSIONS

The foregoing case studies have shown that over the last quarter of a century, isotope methods have been providing an important extra dimension to groundwater investigations in a whole variety of hydrogeological situations.

While isotopic methods have sometimes been sufficient in themselves to explain or resolve questions of groundwater provenance or movement, it must be stressed that in most cases they are not a universal panacea, but must be integrated with physical and chemical data from the groundwater systems in question.

Perhaps the one area in which isotopes are pre-eminent is that of residence time assessment, or groundwater 'dating'. In this regard the radioisotopes tritium (for the short term) and carbon-14 (for the longer term) are currently without competition for any sort of quantitative assessment of age (although groundwater chemistry is important in the interpretation of the latter).

Finally, it can be said that within the constraints mentioned above, isotopic methods have a very considerable role to play in hydrogeological studies of many kinds, and over a whole range of scales. This is particularly the case with investigations of UNSAs, many of which are in areas where inputs of various waters are likely to have strongly characteristic stable isotopic signals (e.g. high-altitude depletion, evaporative enrichment or marine incursion). The two sets of isotopic properties (residence time assessment and groundwater tracing) make such methods a potentially powerful tool in most studies of UNSAs.

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METHOD SUMMARY SHEET (IM 1)

TITLE: Collection methods for environmental isotope samples

Scope and Use of Method

It is important that samples of water for environmental isotope analysis are collected and stored in such a way as to minimise contamination and exchange with the atmosphere. It is also important to collect samples of an appropriate volume. This method sheets deals with these aspects as applied to the collection of O and H stable isotopes, tritium and radiocarbon.

Method

O and H stable isotopes

Stable isotope samples should be collected unfiltered into clean and dry glass bottles with well-fitting, rubber-lined caps. 'McCartney' medical-type bottles are ideal for this purpose and come in 28, 14 and 7 ml sizes. The preferred sizes for collection are the 28 and 14 ml bottles. While samples can be stored at room temperature, care should be taken that the bottle tops are firmly screwed on. In this state, samples have a shelf-life of a year or more.

Tritium

Unless particularly high levels of tritium are anticipated (as are sometimes encountered in pollution plumes associated with nuclear research facilities), a sample of 1 litre volume is required. This should be collected unfiltered into a clean and dry glass bottle with a well-fitting cap. It is essential that possible contamination be avoided; the most likely cause of this is the wearing of older watches whose luminescence is supplied by tritium. Providing bottle tops are firmly screwed on, tritium samples should have a shelf-life in excess of a year. However, from the point of view of radioactive decay it is desirable that they should be analysed as soon as possible after collection.

Radiocarbon

The development of tandem accelerator mass spectrometry (TAMS) in recent years has meant that only a few milligrams of carbon is now required for ^{14}C analysis. In such a case, sample requirements are the same as for tritium: a 1 litre sample in a well-sealed glass bottle.

However, many laboratories worldwide still use traditional counting methods, which require of the order of a few grams of carbon. This frequently necessitates the collection and treatment of > 100 litres of sample. Samples are normally collected in two 60-litre aspirators with drain taps. The samples once collected are made alkaline ($\text{pH} > 9$) and sufficient BaCl_2 added to precipitate all dissolved inorganic

carbon. After being allowed to stand for several hours, the supernatant water is drained off and two aliquots of BaCO₃ are recovered and bulked in a single vessel (usually a ~ 2.5 l capacity plastic bottle) with a well-fitting lid. It is essential that at all stages of this process the ingress of atmospheric CO₂ is avoided. At the reagent preparation stage any possible CO₂ contribution should be precipitated out. During the filling of the aspirators the filling tube should be kept below the water surface. On draining, makeup air should be allowed to enter only through a tube containing 'carbisorb' or a similar CO₂ absorbent.

While 1 litre TAMS samples should have a shelf life comparable to stable isotope samples, the alkaline concentrates for traditional counting should be processed as soon as possible in case atmospheric carbon is incorporated during storage.

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