Review: Environmental tracers in arid-zone hydrology

Andrew L. Herczeg · F. W. Leaney

Abstract Application of environmental tracers to arid-zone hydrology over the past several decades is reviewed, with particular reference to the Australian continent. Some notable successes in the application of stable and radioisotopes include identifying arid-zone groundwater as palaeowaters, understanding the importance of episodicity and of large flood events to recharge, and delineating sources of water to vegetation. Estimating the rates of recharge and discharge have relied to a large extent on chloride and tritium profiles in the unsaturated zone, while radiocarbon and chlorine-36 are used to estimate horizontal flow rates. A number of new research opportunities are suggested. Improved understanding of processes that modify isotopic signatures at the interface zones such as the upper 5m of the soil zone, the capillary zone, and the discharge zone, are needed to better quantify water fluxes across these zones. Furthermore, linkages between the atmosphere-soil-water-vegetation continuum although qualitatively understood, elude quantitative transfer to a scale commensurate with basin-scale groundwater management. The new generation of improved and more robust stable isotope and radiometric dating techniques, will be invaluable in advancing the science and its application to better management of meagre water resources in dry parts of the world.

Keywords Australia · Review · Environmental tracers · Groundwater recharge · Arid zone

Introduction

About 30% of land area on the Earth is arid or semi-arid where potential evapotranspiration exceeds rainfall (McKnight and Hess 2000). These areas, collectively called ‘the arid and/or semi-arid zone’, constitute much of the Earth’s land between latitudes 18 and 40° north and south of the equator and include most of northern and southern Africa, the Middle East, western USA and the southern areas of South America, most of Australia, and large parts of central Asia and even parts of Europe (NOAA 2010). In these environments, low rainfall leads to correspondingly low and intermittent surface runoff and groundwater is often the only reliable water resource. In the current context of ongoing drought in many parts of the globe and the prospect of climate change, the arid/semi-arid zones of the globe may become even drier (e.g., “Climate model simulations for the 21st century are consistent in projecting precipitation ..... decreases in some subtropical and lower mid-latitude regions (likely)”; Bates et al. 2008). Ensuring sustainability of water resources in such areas requires a quantitative estimate of water-balance parameters such as recharge, discharge and rates of horizontal and vertical flow, as well as water residence time. In such regions, the net water flux to groundwaters (defined as recharge) is generally a very small component of the total water balance and conventional approaches are fraught with large uncertainties. In other words, the residual error when subtracting rainfall from evapotranspiration is much larger than the net recharge. Furthermore, monitoring records of piezometric water levels and water quality are restricted to the past few decades and probably do not represent the long-term water balance of arid-zone systems that frequently have water residence times in the range of 10^3–10^5 years.

Alternative methods that involve measurement of naturally occurring isotopic and chemical tracers to estimate recharge, discharge and flow rates for arid-zone groundwater were adopted soon after development of high-precision mass spectrometric and radiometric counting techniques in the 1950s (Aggarwal et al. 2005a). These developments were further accelerated after the atmospheric nuclear weapons tests of the 1950s and 1960s that introduced very large amounts of radionuclides (e.g., ^{3}H, ^{14}C, ^{36}C, noble gas isotopes) into the atmosphere. The resultant rainfall monitoring programs coordinated through the International Atomic Energy Agency (IAEA 2010) have underpinned much of the subsequent work that uses anthropogenic and stable isotopes in hydrology.

One might expect that the fledgling technology and hopes presented in early IAEA meetings (IAEA 1964, 1967), the subsequent compilation of case studies in the

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arid zone (IAEA 1980; Adar and Leibundgut 1994), and numerous case studies in the international literature would by now have developed towards a mature and evolved science. While in the nascent phase of development, the isotopic techniques tended to be used in isolation, and rarely in the form of a comprehensive hydrogeological framework and more often as data gathering or evaluating isotope systematics for their own sake. The purpose of this review is, in part, to evaluate whether there has been any advance on the science since the publication of the last comprehensive review of arid-zone isotope hydrology more than 20 years ago (Fontes and Edmunds 1989). The aim is to compare and contrast environmental tracer work from dry environments with a particular emphasis on groundwater processes and their interactions with ecosystems, evaluate the current state of the science, and identify future research opportunities.

Rather than review the various isotope systematics used in isotope hydrology (see Fritz and Fontes 1980, 1986; Clark and Fritz 1997; Cook and Herczeg 2000; Aggarwal et al. 2005b), the paper has been organized into three themes of arid/semi-arid-zone isotope hydrology:

1. Age and origin of groundwater: past and current flow systems
2. Recharge and discharge: the unsaturated zone
3. Eco-hydrology: groundwater and ecosystems

To some extent, every review represents the biases of the principal authors. In this case, the authors' experiences are largely within the Australian continent. While this may be representative of many other arid regions around the world, it is recognised that factors such as topography, geology and vegetation will cause some differences from place to place. However, the physical laws governing the behaviour of environmental tracers in the hydro-biosphere are universal and therefore the principles should be applicable widely. Furthermore, rather than attempt a comprehensive review of all possible isotopic and chemical tracers used in the arid and semi-arid zone, focus is on the most widely used stable (Cl, $^{2}H/^{1}H$ & $^{18}O/^{16}O$) and radioactive (^{14}C, ^{36}Cl, ^{3}H) environmental tracers.

Palaeohydrology and groundwater flow systems in the arid zone

Palaeohydrology: Are arid-zone groundwater resources renewable?

High-quality groundwater resources in arid and semi-arid zones are often thought to be largely derived from relatively higher recharge regimes during past wetter climates. Much of the evidence for this relies on the observations that groundwater stable isotope compositions ($\delta^{18}O$ and $\delta^{2}H$) are more negative than those of weighted-mean contemporary rainfall (Gat and Issar 1974; Issar et al. 1984). Gat 1983 presents data from groundwater in Israel (Fig. 1a) that show that palaeowaters are depleted in ^{18}O and ^{2}H relative to modern waters in the same region. Moser et al. (1983) show that palaeowaters from arid areas in Saudi Arabia and North Africa (Fig. 1b) lie on a so-called palaeowater line that is parallel to the global meteoric water line (GMWL) and depleted in ^{18}O and ^{2}H relative to modern rainfall. Other studies have shown that there is a progressive decrease in the stable isotopic composition with increasing age along the inferred groundwater flow path (Love et al. 1994; Guendouz et al. 2003). The results from noble gas analyses in arid-zone groundwater have provided additional constraints on the

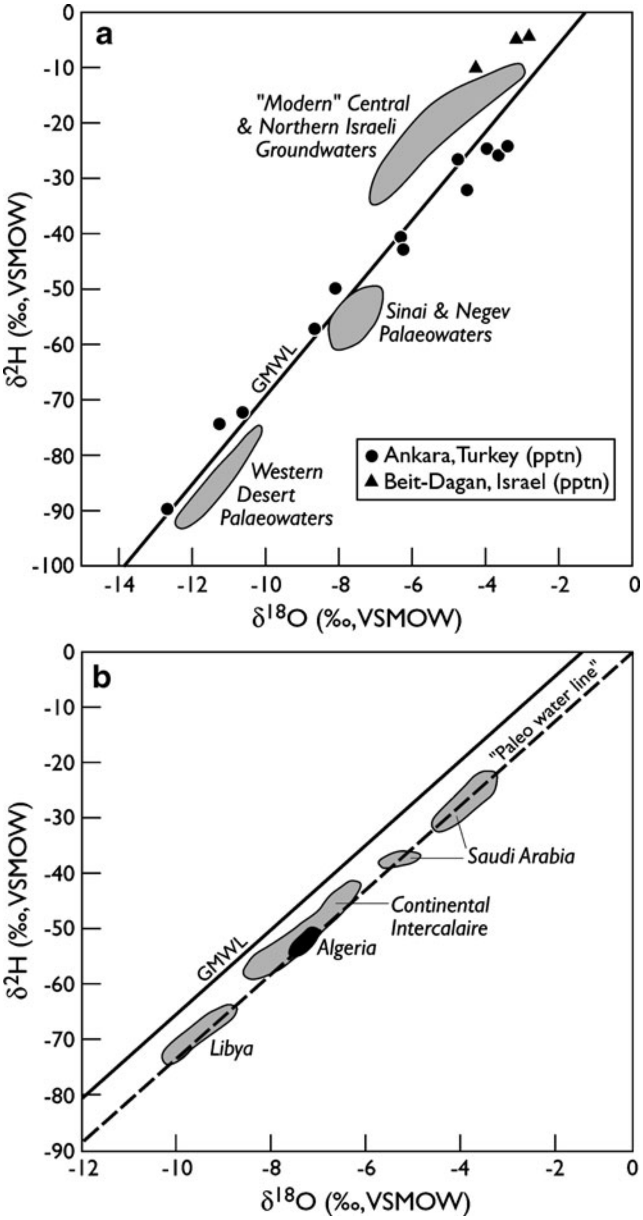

Fig. 1 **a** Stable isotopic composition of modern groundwater and palaeowaters from Israel and Egypt (modified from Gat 1983). Also shown is precipitation (pptn) from Ankara, Turkey and Beit-Dagan, Israel and the global meteoric water line (*GMWL*). **b** Stable isotopic composition of palaeowaters from North Africa and Saudi Arabia (modified from Moser et al. 1983). Also shown is the inferred palaeowater line and GMWL

mechanisms of recharge to fresh groundwater resources in southwestern USA (Stute et al. 1992), North Africa (Andrews et al. 1994; Beyerle et al. 2003) and the Arabian Peninsula (Weyhenmeyer et al. 2000), which have identified changes to storm tracks and weather patterns in these areas similar to those observed in central Europe today.

Interpretation of the isotope hydrochemistry of palaeowaters presents a difficult problem because it must be done completely by inference, based on knowledge of the present day or relatively recent regime. For example, use of the world meteoric water line (WMWL) as a reference for stable isotopes may be biased in both space and time. The WMWL is based on worldwide stations (information is freely available through the IAEA website—IAEA 2010), most of which are in Europe, many of which are coastal, and all of which represent data for, at most, the past 50 years (Araguás-Araguás et al. 2000). The local meteoric water lines for given areas are based on actual data from bulk monthly precipitation, and are usually not precipitation weighted on an annual or longer-term basis. Inferring palaeoclimatic changes from stable isotope data of groundwaters that were recharged thousands of years ago, and comparing that groundwater with recent rainfall, may be flawed when referring to recharge in a wetter or colder climate based simply on an observed ‘lighter’ isotopic signature as discussed in the previous section. In identifying palaeowaters, a change in the “*d*-excess” parameter is a more robust characteristic than simply a more negative $\delta^{18}O$ value (Gat 1983).

Further to the previous section, interpretation of stable isotope data in terms of palaeoclimate signature alone as applied to the arid zone may at times be too simplistic because there are myriad processes that can alter the isotopic signature of rainfall before it reaches the water table (Gat and Tzur 1967; Gat 1987, 1991). For example, altering the seasonality of rainfall (i.e., from winter to summer dominated) will change the isotopic composition of recharge due to the tendency for more rainfall to be lost to the atmosphere in summer than in winter (Fontes 1994). The observed isotopic variability in arid-zone groundwater can be interpreted equally well by spatial and temporal variability in the relative amount and extent of direct or indirect recharge. The former, being infiltration through the soil, is subject to evaporation through the upper part of the unsaturated zone and through transpiration. Indirect recharge, on the other hand, occurs through rivers and flash flooding, where isotopic ratios can be highly depleted in heavy isotopes due to the amount effect. An increase in the predominance of flash floods, rather than evenly distributed rainfall recharge, will also be manifested in more negative groundwater isotopic signature rather than reflecting higher overall humidity. Interpretation of groundwater stable isotope signatures in arid zones are ambiguous because of the large variability in input compositions, the modifications to the isotopic signature at the land surface and during passage through the unsaturated zone yields yield a far greater range of possible final values than those imposed by palaeoclimatic variability. Given that our knowledge is based on relatively recent observations, one must either make assumptions that conditions remained constant throughout the past, or otherwise apply proxy measurements in the palaeo-record to infer the input parameters.

Two examples that illustrate the preceding are presented from the arid and semi-arid zones in central and south-eastern Australia (Fig. 2a). The first of these from the Ti-Tree basin (Fig. 2b) from the arid zone of central Australia (rainfall=290 mm/a; potential evapotranspiration (PET)=3,030 mm/a) where the stable isotope signatures of groundwater are very depleted compared with the annual weighted-mean rainfall (Fig. 3). A line through the data points extrapolated to the WMWL is interpreted as being the result of recharge to the groundwater via predominantly heavy rainfall events (150–200 mm/month) that is partially evaporated within the soil zone prior to recharging the water table. If one compares the data from Ti-Tree basin with the semi-arid-zone Mallee area of SE Australia (Fig. 2c; rainfall=275 mm/a; PET=2,150 mm/a), each region displays relatively uniform stable isotope composition (Fig. 4) but very different to each other despite similar annual rainfall. All waters lie to the right of the local meteoric water line (LMWL), and are depleted in ^{2}H and ^{18}O compared with weighted-mean modern rainfall from the respective areas, but the groundwater in the Ti-Tree basin shows much greater depletion in heavy isotopes (and much lower salinity; data not given) than in the semi-arid Mallee system. These results can be interpreted as partial evaporation of rainfall in the soil zone prior to recharge, and the isotopic composition at the line of best fit through the groundwater data to the LMWL is the weighted-mean rainfall amount contributing to recharge. The data suggest that arid areas, with rainfall of 150–300 mm/a may have higher recharge rates than semi-arid areas, which have permanent vegetation where recharge rates can be <1 mm/a. Because vegetation, and to a lesser extent soil type, is a key driver of the recharge fluxes to groundwater, and removal of water by plants does not fractionate isotopes, but does fractionate salt by 100%, the combination of isotope and chloride data is a very powerful tool to delineate recharge processes in the arid/semi-arid zone without necessarily needing to invoke climatic change to explain the isotope shifts.

Very often the isotopic signal is smeared and altered by mixing or sampling from boreholes with long well-screen intervals where the signal may incorporate numerous wet and dry climatic periods making it difficult to resolve isotopic signatures for use in water resources management. It cannot be overemphasized that a well-constrained hydrogeological conceptual model adds enormously in such situations where the environmental tracer data alone is ambiguous. The resolution of these palaeoclimatic changes may be improved by isotopic profiles of soil-water and soil gas in the unsaturated zone as they provide high-resolution information that can be extrapolated to the regional groundwater scale (e.g., Cook et al. 1992; Tyler et al. 1996; Thorstenson et al. 1998; Edmunds and Tyler 2002; Walvoord et al. 2002).

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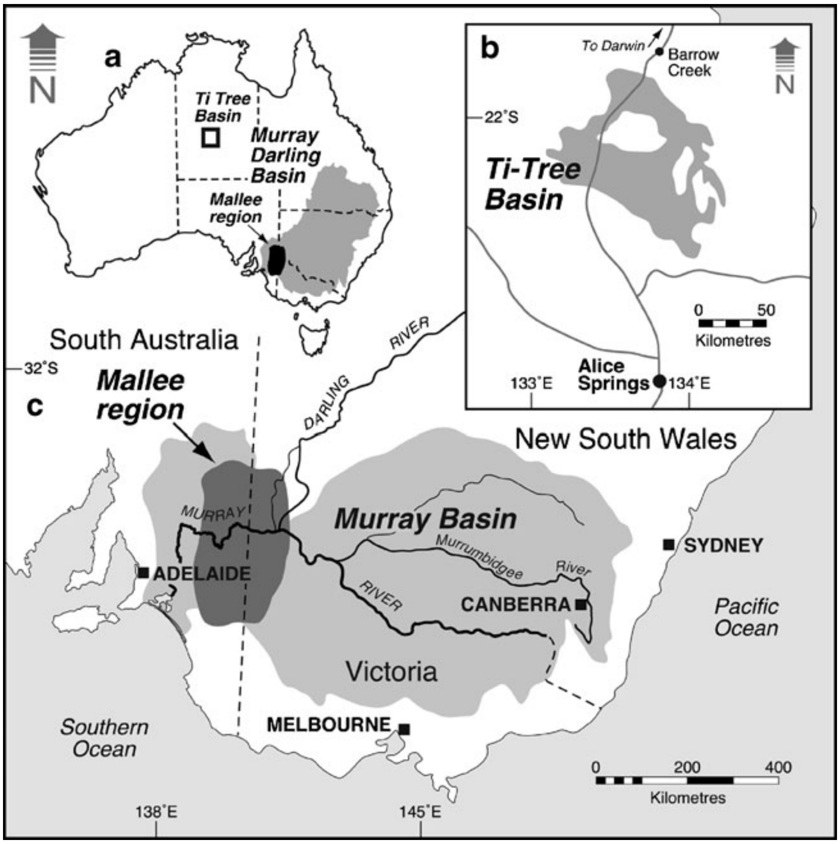
Fig. 2 **a** Location map of the two study sites in Australia; **b** detailed map of *Ti-Tree basin*; **c** detail of location map of the *Mallee* area in the western Murray Basin, SE Australia



Recharge and discharge estimates from groundwater flow rates/ages

Because of the increasing concern about sustainability of arid-zone groundwater resources, there is a need to know the past, present and future water-balance parameters to determine whether or not the aquifer system is in hydro-

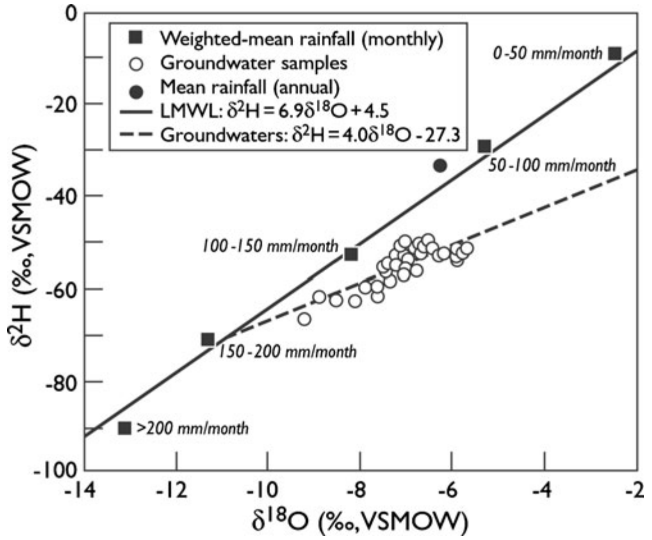


Fig. 3 Compiled stable isotopic composition of rainfall from Alice Springs, central Australia (IAEA 2010) organized on the basis of monthly amount showing the heavy isotope depletion with increasing rainfall amount. Also plotted are groundwater data from the Ti-Tree basin, (see Fig. 2 for location) extrapolated back to the local meteoric water line (*LMWL*) (modified from Harrington 1999)

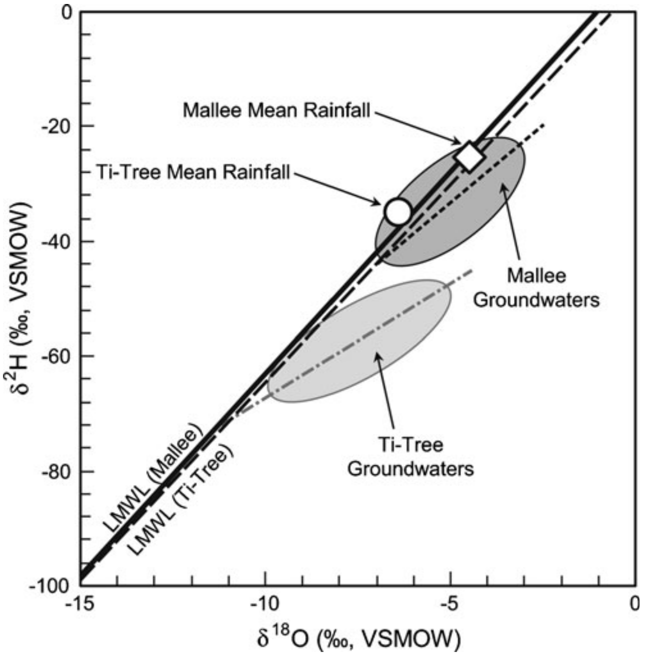


Fig. 4 Comparison of approximate distribution of stable isotope data from the *Ti-Tree* basin (central Australia) and the *Mallee* region of the SW Murray Basin (SE Australia). Also shown is the local meteoric water line (*LMWL*) for both sites (Ti-Tree data from Harrington 1999; Mallee data from Herczeg et al. 2001)

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logical steady-state (i.e., Does recharge equal discharge?). Estimates of recharge to, and discharge from arid-zone groundwaters have involved two main approaches: (1) chemical and isotope profiles in the unsaturated zone (discussed in detail in the following section) and (2) radiometric techniques such as dating of groundwater along inferred flow paths in the saturated zone. Because of the low water fluxes in the arid zone, groundwater systems here tend to be comprised of water with predominantly long water residence times. That is, they have resided in the subsurface on time scales of the order of 10^3 years (local resource) to 10^6 years (regional resource). Dating of groundwater on this time scale is best afforded through measurement of natural radioisotopes such as ^{14}C and ^{36}Cl, having half lives of 5,730 and 301,000 years, respectively (Vogel 1967; Cresswell et al. 1999; Phillips 2000; Zhu and Murphy 2000).

Dating of water in dry areas has a specific set of research problems that are distinct from the usual set of complexities surrounding interpretation of ^{14}C or ^{36}Cl groundwater 'ages' inferred from samples collected along groundwater flow paths (Froehlich and Gat 2001). A major difficulty is assigning an appropriate correction scheme for ^{14}C dating (i.e., estimating the initial ^{14}C concentration at the time of recharge). One of the reasons for this is the variability of chemical and isotopic end-members such as soil gas δ^{13}C, ^{14}C and pCO$_2$, and assigning carbonate mineral δ^{13}C and ^{14}C, which are used in the various ^{14}C correction schemes. Furthermore, the paucity of available boreholes and information that specify depth and length of screens (which sample over different water residence time ranges), and the impact of diffusion where recharge rates are very low (Walker and Cook 1991; Sanford 1997) also increases the level of uncertainty. Solving the first problem involves better characterisation of the various model parameters on a site-by-site basis, as well as better understanding of soil CO$_2$ dynamics in arid zones, particularly modification of the soil ^{14}CO$_2$ signature as it enters the saturated zone (e.g., Thorstenson et al. 1983, 1998; Wang et al. 1994).

Because the concept of a groundwater 'age' is not directly useable in evaluating the water balance, there is increasing consensus that radioisotopes should be used to estimate mean flow rates for confined aquifers (e.g., Love et al. 1994, 2000; Zhu and Murphy 2000), and recharge rates (Vogel 1967; Geyh 1992; Harrington et al. 2002; Herczeg 2007) for unconfined aquifers. The true estimate of mean residence time of groundwater is given by total storage divided by the discharge rate, and not the 'age' derived from the radioisotope 'model' age. The horizontal groundwater flow rate is estimated for confined aquifers (assuming piston flow) by determining an age difference between a sequence of boreholes along a hydraulic gradient, and an approximation of the cross sectional area of the aquifer, and porosity or storage coefficient, to be able to calculate a discharge rate (Love et al. 1994, 2000; Zhu 2000; Sanford et al. 2004).

In the case of unconfined aquifers where flow systems range from local to intermediate, recharge rates (R) can be estimated for various flow paths taking into account depth of the borehole and length of the screened interval (Vogel 1967; Harrington et al. 2002):

$$R = H\lambda\theta.\ln\left(\frac{H}{H-z} - \frac{A_0}{A}\right) \tag{1}$$

where

R	Recharge rate (L/T)
H	Total thickness of unconfined aquifer (L)
λ	Decay constant (T^{-1})
θ	Porosity (L^3)
z	Depth of mid point of screened interval (L)
A	Measured activity of isotope
A_0	Initial activity of radioisotope

Application of Eq. 1 to measured ^{14}C over a large area can yield a range of recharge rates that can be explicitly expressed on a map along inferred flow paths back extrapolated along the hydraulic gradient. Figure 5 shows estimated recharge rates for the arid Ti-Tree Basin of central Australia determined from ^{14}C data. The histogram of corrected 'ages' (Fig. 5a) shows a log-normal distribution, and at face value suggests that most of the water was recharged between 2,000 and 6,000 years ago. However, the sampling depth of bores biases the age distribution, and thus the mean residence time inferred from the ages does not always reflect the basin as a whole. The mean recharge rates shown on the map (Fig. 5b) are variable, as is often the case in arid areas where rainfall variability is very high, but values generally lie between 1 and 5 mm/a. The recharge rates can be related to a number of physiographic factors such as soil type, vegetation and distance from major ephemeral surface drainages. One can either scale up the recharge rates to estimate total input of water to the groundwater system, or use the spatial data to identify localized recharge areas.

Integrating isotopes and hydraulics

Integration of the radiometric data with conventional hydrological information (hydrostratigraphy, piezometric response to rainfall, estimation of flow rates from Darcy's Law) is an essential part of tracer application in the arid zone. Such an approach is necessary to maintain credibility with the end-users of the information, as well as the obvious need to get as many different approaches as possible, and if necessary, to reconcile them. Very often, if there is a discrepancy, this can provide information about changes to recharge over time and/or the physical characteristics of the flow system.

The use of particle tracking models (e.g., Vogel 1967) to evaluate spatial variability of recharge, and also to 'aggregate' recharge has probably been underutilized to date. This accounts for variability in screen length in unconfined aquifers which makes transects and flow path models at best hard to interpret or worse,

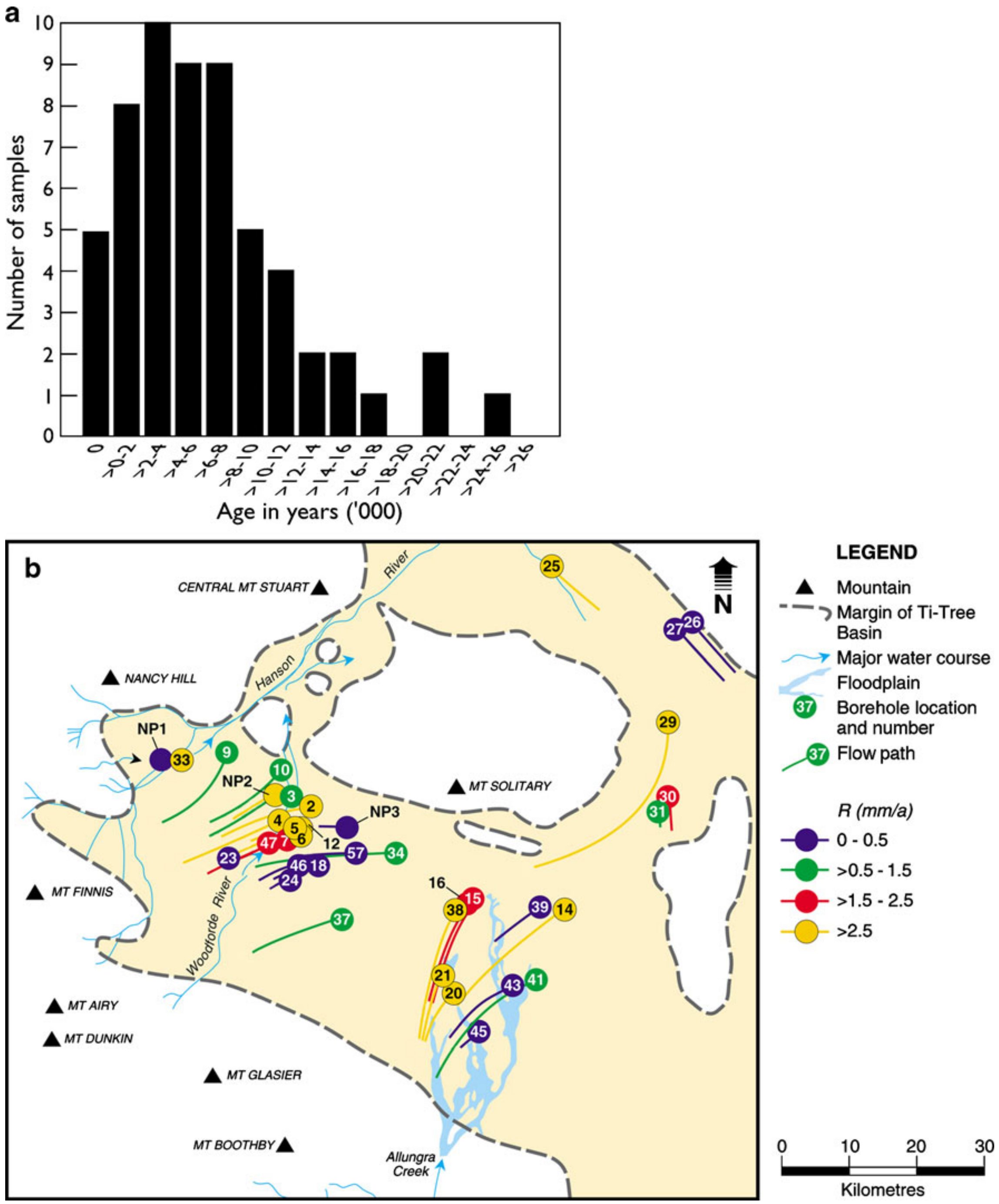

Fig. 5 **a** Distribution of modelled radiocarbon ages for the Ti-Tree basin, central Australia. **b** Distribution of recharge rate estimates (*R*) shown for individual boreholes along inferred flow lines (*shaded solid lines*) determined from screen intervals and aquifer geometry (after Harrington et al. 2002)

misleading and demonstrates the fallibility of the concept of groundwater "age". The incorporation of isotopes into various types of numerical groundwater flow and solute transport models (e.g., Maloszewski and Zuber 1982; Yurtsever and Payne 1986; Zuber 1986; IAEA 1996; Zhu 2000; Sanford et al. 2004) is emerging as a new frontier. In particular, the use of isotopes as a constraint on boundary conditions or other parameters is seen as an area that can be further developed. Greater application can also be made in the use of models to test hypotheses or conceptual models that are based on interpretations of isotopic and chemical data. In other words, isotopic measurements may be used to validate hydraulic models based on basic hydrogeological principles. These may hold special value in the arid zone because of the time lags in response to variable

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recharge rates as well as palaeoclimatic changes throughout the time history of water residence time.

Recharge and discharge estimation (unsaturated zone studies)

Stable isotopes in the unsaturated zone as a tool to estimate recharge and discharge

The unsaturated zone in most areas is the conduit through which rainfall must pass to reach the water table, and the composition of water in the upper few metres can record important information about recharge processes and recharge rates. Models describing the behaviour of $^2H/^1H$ and $^{18}O/^{16}O$ in soil-water profiles undergoing recharge or discharge (Allison and Barnes 1985; Barnes and Allison 1988) were based on the rationale that a steady-state vertical profile would develop, characterised by enrichment of ^2H and ^{18}O in the upper part of the soil profile. Removal of the lighter isotopes of water through an upward water flux due to evaporation would be balanced by downward advection or diffusion of the heavy isotopes. Thus, one could potentially estimate the recharge or discharge flux from the degree of heavy stable isotope enrichment, as well as depth of the evaporation front.

Numerous field profiles in semi-arid and arid environments (e.g., Fig. 6), have verified the theoretically predicted results, but relatively few attempts have been made to use the data to quantify recharge rates. Although the science of unsaturated-zone-soil-water dynamics and stable isotope systematics is advanced, a practical use is not self-evident. Allison et al. (1984) suggested a relationship between deuterium deficit (δ^2H-m^{18}O, where m is the slope of the local meteoric line) and recharge rate (Fig. 7a, Eq. 2) where:

$$\text{Deuterium deficit } \alpha \ (\text{Recharge})^{1/2} \tag{2}$$

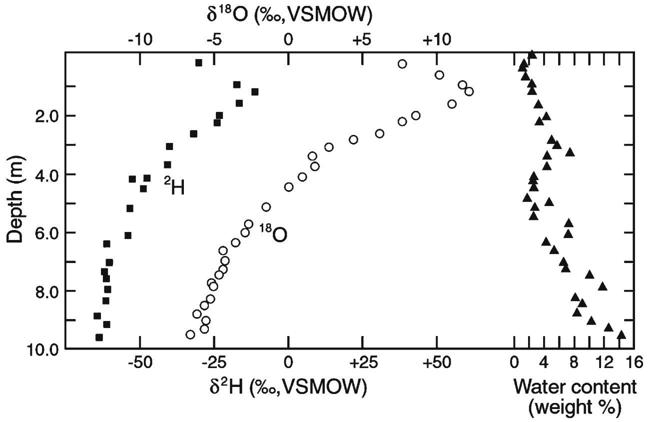

Fig. 6 Soil-water-stable-isotope profiles in the Sahara (after Fontes et al. 1986) showing the classical enrichment of ^2H and ^{18}O in the upper 2 m of the soil profile

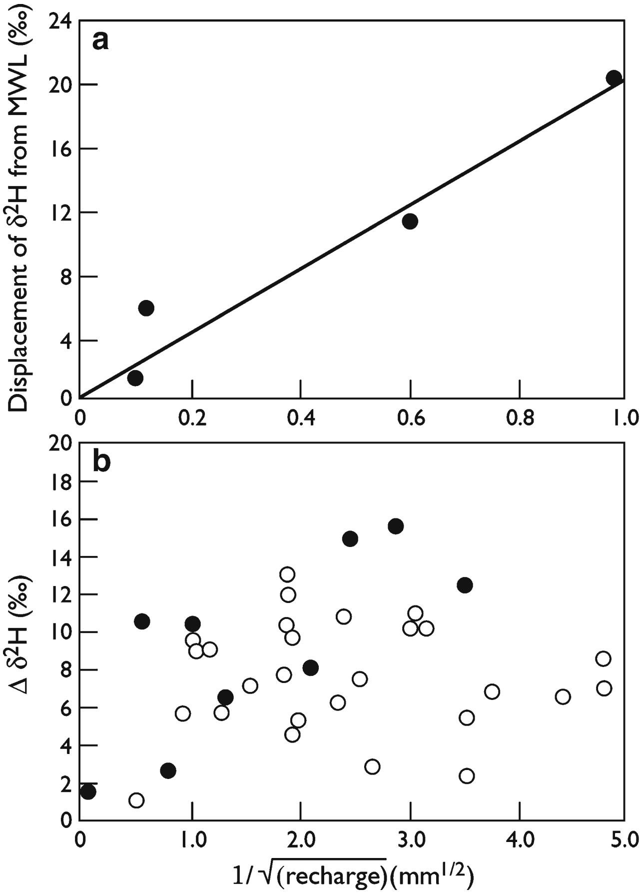

Fig. 7 Soil-water-stable-isotope data from SE Australia soil-water profiles plotted in terms of displacement of ^2H from the meteoric water line as a function of the square root of recharge rate. **a** Shows the initial data from Allison et al. 1984; **b** shows subsequent data with *solid circles* showing early data and *open circles* showing subsequent data (G.B. Allison, CSIRO Land and Water, unpublished data 2000)

This initial relationship, however, was not borne out at other sites (Fig. 7b; initial data shown as closed circles, more recent unpublished data as open circles). The likely reasons for lack of general applicability are:

1. The impact of vegetation, which affects recharge through removal of water from the soil but has no effect on isotopic signatures (the theoretical derivation is based on water loss from the soil by evaporation alone and not transpiration)
2. Seasonal variation in the δ^2H and $\delta^{18}O$ composition of rainfall

While the use of stable isotopes as a quantitative tool in recharge studies may not have lived up to earlier expectations, there has been much more robust application of discharge estimation using the δ^2H and $\delta^{18}O$ composition of soil water. The method is applicable when there is a net discharge from a site and the impact of precipitation does not penetrate significantly into the soil profile. Estimates of discharge can be made by analysing the quasi-exponential shape of the enriched isotope profile (Sonntag

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et al. 1980; Fontes et al. 1986; Barnes and Allison 1988). Even so, there has been little uptake of the methodology by the water-management agencies of this technique, and of isotopic techniques in the unsaturated zone in general.

Two of the limitations for the use of isotopic measurements in recharge/discharge studies include difficulties and relatively high cost in collecting soil-water core samples and analysing samples, and uncertainties when extrapolating the results from single soil cores to regional areas that can directly make an impact on groundwater management. Estimation of recharge and discharge rates in arid and semi-arid environments using chloride mass balance approaches (see section Recharge estimates by chloride mass balance) provide a more quantifiable estimate for recharge rates than that using δ^2H and δ^{18}O. However, the isotopic data, in conjunction with soil-water chloride, provided a parallel understanding of recharge processes such as episodic versus continuous recharge, and the potential for by-pass flow, as opposed to piston flow, for many soils in arid environments.

Recharge estimates by chloride mass balance

The application of chloride ion as a tracer in conjunction with isotope studies in the arid zone is so ubiquitous that it deserves some review here. Much of the mathematical treatment of Cl^- in soil profiles is similar to that of stable isotopes, and because of its solubility, is a near proxy for movement of water. Evaporation and transpiration completely excludes Cl^- which is concentrated quantitatively and all the Cl^- remains in soil water. In the absence of significant surface runoff, one can estimate recharge simply by the product of mean annual rainfall, Cl^- in rainfall divided by the Cl concentration in the soil water at the plant root zone (or Cl_R^-) via rearrangement of Eq. 3:

$$PC_{\mathrm{p}} = RC_{\mathrm{R}} \tag{3}$$

Where

P Precipitation (L/T)
C_{P} Cl^- Concentration in rainfall (M/L^3)
R Recharge rate (L/T)
C_{R} Concentration of Cl^- in recharge (M/L^3)

Since the pioneering work of Eriksson and Khunakasem (1969) and Allison and Hughes (1978) a number of workers throughout the world have used Cl^- in both the unsaturated and saturated zone (see reviews by Allison et al. 1994; Wood and Sanford 1995; Herczeg and Edmunds 2000; Scanlon et al. 2006), though some caution should be exercised when dealing with certain environments which show evidence for by-pass flow (Wood 1999; Scanlon 2000). Recharge estimates using point source data from the unsaturated zone profiles demonstrate the spatial variability at the plot scale due to variation in land-scale parameters; stable isotope profiles provide additional confirmation of the recharge processes and the use of tritium corroborates the piston-flow mechanism as well as the timescales. There appear to be significant differences in chloride profiles in the unsaturated zones of arid regions in Africa, the USA and Australia which reflect the differences in landscape characteristics as well as global location. While residence times in African profiles measured to date generally do not exceed 1,000 years (e.g., Gaye and Edmunds 1996), in Australia and North America, profiles recording recharge events over many thousands of years may be found (Allison et al. 1985a; Scanlon 1991, 2000; Stone 1992; Tyler et al. 1996; Phillips 1994; Leaney et al. 2003; Scanlon et al. 2003). In Australia, the soil-water chloride concentrations measured beneath water-efficient native mallee-form vegetation usually reaches a maximum at a depth of 5–10 m (Allison et al. 1985b).

Chloride profiles in the unsaturated zone can take on a number of characteristics depending on depth to water table and groundwater chloride concentration. There may be a pronounced bulge if the groundwater Cl is low (Fig. 8a) or the concentration could be maintained throughout the unsaturated zone (Fig. 8b) if the salinity of groundwater is the same as that of the steady-state-soil-water concentration. For deep water tables, there may be a large zone of diffusion resulting from vapour transport in deep soils (Fig. 8c). In the semi-arid areas studied in Australia, the terrain is relatively flat with minimal run-on, and the mallee-form vegetation is deep-rooted and able to reach high levels of stomatal potential to enable withdrawal of water from soil water with a high osmotic potential. The initial interpretation of this is that recharge rates in the areas studied in Australia (SE Australia) have been consistently low for periods of many thousands of years (up to 40,000 years assuming present day rates for chloride accession).

However a number of cumulative water versus cumulative chloride profiles from the Mallee area of SE Australia (Fig. 9; location shown in Fig. 2) show a range of trends that reflect a combination of recharge rates at different local environments (reflecting soil type, vegetation, etc.) as well as changes to these fluxes in response to changing climate as shown by a break in slope (Leaney et

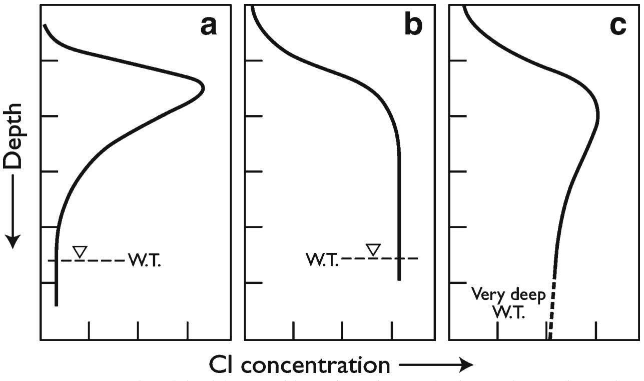

Fig. 8 Generic chloride profiles showing **a** bulge where there is a maximum extraction of water via transpiration, and diffusion to a lower-salinity groundwater with a shallow water table (*W.T.*), **b** no bulge where groundwater salinity is the same as soil-water salinity, and **c** very deep soil profile showing a less pronounced bulge due to vapour exchange over long time frames (modified from Phillips 1994)

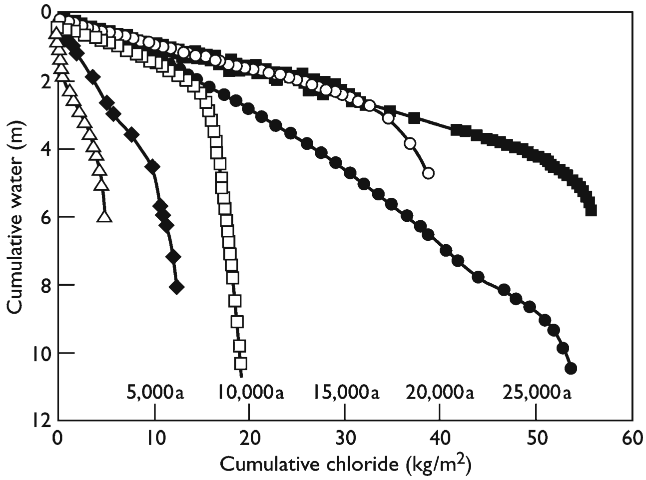

Fig. 9 Cumulative chloride versus cumulative water content for a range of soil types and climatic areas in the Mallee area of the semi-arid zone of SE Australia (see Fig. 2 for location; modified from Leaney and Herczeg 1999)

al. 2003) on a time scale over the past 25,000 years. Models of vertical vapour movement in very low recharge unsaturated zones (Walvoord et al. 2002) show that palaeoclimatic data can be extracted despite other physical processes that combine to smooth out long-term climatic information on changes to recharge fluxes over time. The cumulative Cl^- flux method may be used, therefore, not only to estimate long term (decadal) recharge rates, unobtainable by classical methods, but also, under favourable circumstances, the recharge and climatic history (Edmunds and Tyler 2002).

Eco-hydrology

Plant-water sources

The use of the δ^2H and δ^{18}O composition in plant water has provided critical data for determining the source of water use by vegetation, for example soil water versus groundwater (Dawson and Ehleringer 1991; Ehleringer and Dawson 1992; Brunel et al. 1995). It is increasingly being recognized that groundwater-dependent ecosystems in arid areas are very susceptible to small changes in water level. Use of groundwater by phreatophytic vegetation is increasingly being acknowledged during extended dry periods. Water-level data from dryland areas are often either sparse or non-existent. Therefore, policies that provide so-called 'environmental water' are often difficult to justify and implement because of the unknown amount of water that is required to maintain ecosystems during prolonged periods of drought. To do this, it is necessary to know whether plants are accessing water solely from shallow soil water or whether deeper soil water or groundwater is being used. One of the approaches to this involves comparing the isotopic signature of plant water (extracted from twigs) with that of the potential water sources.

As with many isotopic applications, it is necessary to use other data such as soil water and groundwater salinity (osmotic potential) and soil-water potential to confirm the results from the isotopes. In other words, water sourcing via an isotopic investigation may suggest a single, or more often, multiple water sources for the vegetation (Fig. 10). Soil physical and chemical evaluation confirms whether the results are sensible. The use of isotopes is seen as complementing other studies to provide added confidence in the conclusion (Walker et al. 2001). Isotopic investigations of this type have been very illuminating in showing the many and varied ways that plants adapt to the hostile arid environment. For example, in addition to being able to maintain a high stomatal potential, many trees and shrubs in arid regions are able to send roots to depths of 30 m or more and extract lower salinity water from the capillary zone during periods of drought. The vegetation must expend energy for these deep roots to survive during periods when low salinity/low soil potential soil water is available at shallower depths. However, by expending this energy during periods when soil water

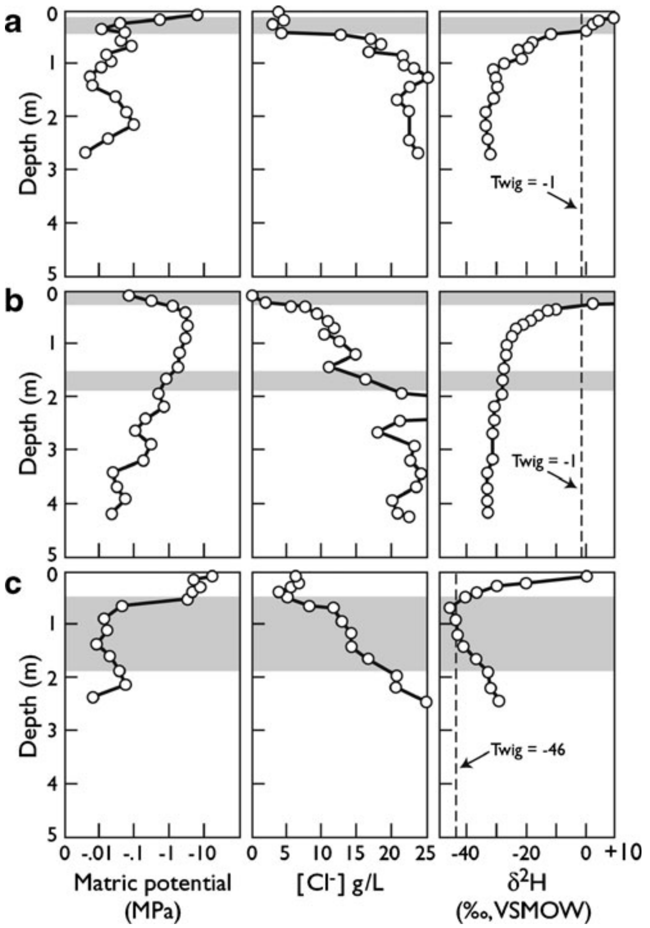

Fig. 10 Soil matric potential (*left panel*), soil water chloride concentration (*middle panel*), and deuterium composition of soil water (*right panel*) for three sites (**a**–**c**) in the semi-arid Murray Basin, Australia (modified from Brunel et al. 1995). The *shaded areas* indicate plant water-source uptake region and the *dashed line* indicates plant-water composition

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is available, the plants are then able to tap into water from the capillary zone during prolonged drought (Brunel et al. 1995).

Vegetation, recharge and climate

The last decade has seen an increase in awareness and concern over the impact of groundwater use on groundwater-dependent ecosystems such as baseflow to rivers and phreatophytic vegetation that may be affected if groundwater levels are altered. The small residual of the water balance in arid areas is the result of complex feedback between the biosphere-hydrosphere and atmosphere and manifests itself as groundwater recharge. Recharge variability in space and time is particularly pronounced in such regions. The quality of data on climate variability ranges from very precise recent rainfall and temperature records over the past 100–200 years to millennia, for which records are incomplete and with much lower temporal resolution. The detailed understanding of isotopic systematics in these interactions is well advanced (e.g., Gat 1996).

One of the questions often posed is: “Is there a threshold of rainfall amount at any particular environment before any significant recharge occurs?” In native-vegetation-covered areas in the semi-arid environment of SE Australia, where winter rain is the norm, the threshold is probably around 400–500 mm/a for sandy soils, and 100–200 mm/a more for loam and heavier textured soils. In the more arid regions in the US, threshold values are considerably lower, probably as a result of the potential for run-on because of the more mountainous terrain and because the vegetation is less water efficient (Phillips 1994). Generalisations such as these, because they are based on a large knowledge pool of field investigation, may be worthy of further investigation to help develop improved conceptual models of recharge processes in arid environments.

Summary and future opportunities

Environmental tracer techniques have been shown to provide both qualitative and quantitative information on hydrological processes in the arid/semi-arid zones, particularly with respect to groundwater. Some examples articulated above: (1) stable isotopes of water in conjunction with ^{14}C demonstrate that many arid-zone groundwaters are palaeowaters, and are recharged often episodically through a number of different mechanisms, (2) long-lived natural radionuclides such as ^{14}C and ^{36}Cl are used routinely to estimate recharge and horizontal flow rates on a regional scale, and provide information that is not easily obtained through conventional hydrogeological approaches, (3) unsaturated-zone studies using stable isotopes, chloride mass balance and tritium have provided estimates of very low rates of discharge and recharge respectively, (4) combined use of stable isotopes and soil physical properties have been used to evaluate sources of water taken up by desert vegetation, which is a key component of the burgeoning field of eco-hydrology.

However, some of the early aspirations of isotope applications in the arid zone may have not have been fully realised. Recharge estimation using stable isotope data from the unsaturated zone and the application of more recently developed isotope techniques has limited applicability. The degree of success is to some extent a function of the degree of intractability of the problem and that arid-zone hydrology usually poses very difficult questions. Chloride mass balance (or mass accumulation) remains the cornerstone of recharge estimation in the arid zone, despite limitations inherent in the method. Uncertainties in Cl input rate over time, validity in the assumption of piston flow, the influence of upward fluxes of water vapour, and discrepancies between recharge estimates from saturated zone data which are frequently lower than those from unsaturated zone estimates, all impose constraints and uncertainties. Many stable isotope methods remain largely qualitative and future developments are likely to be in areas that are suitable for development of more quantitative approaches.

Systematic comparisons of data sets from different parts of the world could improve the understanding of the overall factors controlling recharge/discharge. This may not necessarily lead to a comprehensive “unifying” paradigm (which is unlikely in such complex systems) but provide proxy, widely available datasets (such as soil characteristics in the upper few metres of the unsaturated zone) that are amenable to being applied at regional scales, which is useful for water managers. For a given climatic regime but very different topographic setting, recharge rates and mechanisms and flow systems in low topographic environments (e.g., Australia) are likely to be different to that of groundwater basins of high relief (Israel, western USA). Evaluating whether there are particular thresholds or non-linear response to forcing functions (such as rainfall amount, vegetation density, elevation gradients, etc.) will also be needed if there are to be simple models that relate current short term (10^{-2}–10^{2} years) observational records (e.g., rainfall amount, remote-sensing data, future climate models) to long-term groundwater recharge (10^{2}–10^{4} years).

Nested studies at spatial scales ranging from 10^{-1} to 10^{5} m are needed at a given basin, rather than an ad hoc data-gathering exercise from one place to another. Usually, there are either basin-scale studies (e.g., borehole and well sampling programs) instituted by water-management agencies or very fine-detailed studies that test specific process models (e.g., detailed soil profiles) designed by research agencies. Very rarely are systematic field programs undertaken designed to link processes from the point study through to the whole basin or sub-basin (Andrews et al. 1994; Harrington et al. 2002).

Much of the environmental tracer information is imparted or modified at key interface zones: (1) the upper 5 m of soil, (2) the capillary zone, and (3) the discharge zone. These zones are often characterised by large gradients in water content, salinity and oxygen (and other redox species) concentrations. While they have been studied extensively in some areas of the world, and are well understood qualitatively, quantitative information on water fluxes is still not well constrained.

New groundwater investigations should, as much as possible, include pore-water profiling during drilling. This allows research into vertical profiles through the saturated and unsaturated zone. It also helps with distinguishing between processes such as groundwater chemical and isotopic evolution (via rock–water interaction) as opposed to mixing. The added cost of obtaining pore fluids, though not insignificant, yields much more knowledge than that obtained through opportunistic sampling of boreholes of unknown sampling interval and depth.

Much of the arid zone is underlain by karstic or fractured carbonate or silicate aquifers where very little research has been carried out compared with porous media. The main reason that they have been avoided is because research in these areas is very complex, and observational data can confound conventional interpretation approaches. For example, fractured rocks have very low porosity but high hydraulic conductivity in <1% of the bulk aquifer (Cook 2003). In these systems, sampling in different ways can give conflicting results (e.g., diffusion cells; piezometers; pump-packers in open boreholes). Environmental tracer techniques may provide the best avenue for success because of their tendency to integrate spatial and temporal variability, and retain the imprint of the hydrological history.

Finally, interest in application of tracer techniques to new technologies and problems in the arid zone such as managed aquifer recharge, improving irrigation efficiency and surface-water/groundwater interactions, is gathering momentum. The demand for much more intensive sampling frequency in some studies may now be realised by some of the new generation of optical water-isotope measurement techniques (Kerstel 2007) and other on-line mass spectrometric techniques (e.g., continuous flow pyrolysis) which can very quickly generate very large numbers of analyses at the level of precision suitable for constraining end-member isotopic compositions that were otherwise too labour intensive to be practical.

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