

[1]

## EXAMINING EVAPOTRANSPIRATION IN A SEMI-ARID REGION USING STABLE ISOTOPES OF HYDROGEN AND OXYGEN

C.D. WALKER<sup>1\*</sup> and J.-P. BRUNEL<sup>2</sup>

<sup>1</sup>CSIRO Division of Water Resources, PMB 2, Glen Osmond, S.A. 5064 (Australia)

<sup>2</sup>ORSTOM, Department TOA, 213 Rue La Fayette, 75480 Paris (France)

(Received September 11, 1989; accepted for publication October 2, 1989)

### ABSTRACT

Walker, C.D. and Brunel, J.-P., 1990. Examining evapotranspiration in a semi-arid region using stable isotopes of hydrogen and oxygen. *J. Hydrol.*, 118: 55-75.

Daily variation of the isotopic composition, both deuterium and oxygen-18, of water in foliage of a mixed *Eucalyptus foecunda* - *Eucalyptus socialis*, 'mallee' community was studied in relation to the isotopic composition of soil water and atmospheric water vapour, transpiration and evapotranspiration, and environmental conditions.

The isotopic composition of water in foliage and the soil surface were enriched over adjacent stem and deeper soil water respectively, characteristic of water subject to evaporation. The composition of foliar water varied systematically over the day, being highest in the late afternoon, in response to lower relative humidity.

The foliar water composition fitted a steady-state model of leaf water fractionation. It was found that the fraction of leaf water equilibrated with the atmosphere was at a minimum during the middle of the day, fitting earlier observations of an inverse correlation of this fraction with transpiration rate. The equilibrated fraction was relatively high compared with previous transpiration studies, consistent with low transpiration rates. The soil water isotope-depth profiles had not achieved steady state. Using existing models, we conclude that the foliage and soil compartments are exchanging water vapour, but that some complicated evaporation processes are occurring in the soil, probably as a result of daily temperature cycling.

Examining the relationship of the two isotope tracers in the different compartments, the vapour transport fits a transport model in which it is strongly diffusion-limited, both within the soil and leaf. Because of some uncertainty as to the transport mechanisms involved, it is not clear what the relative contributions from soil and foliage are. The vegetation may be having a considerable influence on the total evaporation from the community, since the effects of the root system on the soil structure and soil water transport are not clear.

### INTRODUCTION

Bariac et al. (1983) proposed that the isotopic composition of water in the soil-plant-atmosphere continuum may be used to estimate the proportion of the water vapour contributing to evapotranspiration (ET) from different sources. The *Eucalyptus* mallee communities of southern Australia are typical

\* Present address: Queensland Wheat Research Institute, P.O. Box 2282, Toowoomba, Qld. 4330, Australia.

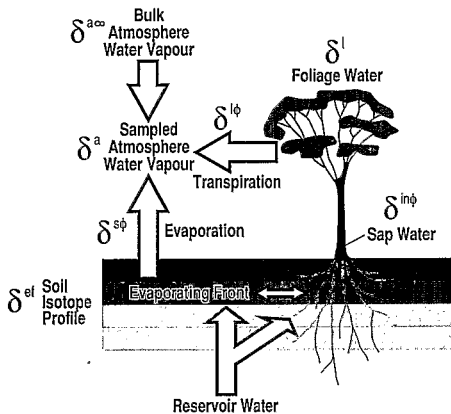


Fig. 1. Schema of plant and soil evaporation. Evaporation at the soil evaporating front results in its enrichment in deuterium and oxygen-18 isotopes owing to different physical properties of the heavy water. Enrichment also occurs in foliage.

of many in semi-arid regions in that they have discontinuous canopies. This structure leads to considerable complications in the study of ET since basic parameters such as temperatures, radiation and wind speed vary considerably in the horizontal plane, and water vapour may be derived from foliage or bare soil. Further techniques to improve estimation of ET in such environments, such as that proposed by Bariac et al. (1983), would be of considerable value.

An examination of a soil-plant (tree)-atmosphere system (Fig. 1), shows the dominant compartments of water that may be distinguished by their isotopic composition and the fluxes of water between these. The evaporation phase change and vapour diffusion causes enrichment of liquid phases in foliage and soil, while the associated vapour fluxes are relatively depleted. It may be considered that both evaporating surfaces (soil and foliage) derive water from a deep source, when at near steady-state conditions. This reservoir is of the same composition as the rain events that provide infiltration (or very similar to these since it may also receive a minor contribution from the enriched soil water).

At any time, the isotopic composition of sap water of a tree may be more enriched than the deep reservoir water, since the root system may obtain water from the partly enriched water in the shallower part of the profile (arrow in sub-soil, Fig. 1). Over time, transpired water vapour has an average composition equal to the plant sap water (Zundel et al., 1978; White, 1983). Consequently, the vapour transpired by the leaf will be similarly enriched when compared with reservoir water. On the other hand, until the soil water isotope profile is fully developed, the isotopic composition of soil vapour will be less enriched than the soil source water, since the development of the profile involves the retention of the heavier isotopes. The soil surface proceeds to an equilibrium composition at a far slower rate than foliage (Walker et al., 1988). When an overall steady-state is eventually achieved, the ET flux should have the same composition as the source reservoir.

This paper examines the isotopic composition of water in the major parts of

the soil-plant-atmosphere continuum in a *Eucalyptus* mallee community. The natural retention of deuterium and oxygen-18 compared with the lighter isotopes in liquid water during evaporation results in varying isotopic compositions in different compartments (atmosphere, leaf, stem, soil). This also influences the isotopic composition of the vapour fluxes between these compartments, and we discuss these in light of the inter-relations suggested above.

The model estimating the intermixing of vapours of different composition from different sources, after Bariac et al. (1983), is described. It is observed that the simple mixing model is inadequate because of diffusion effects, with compositions fitting a more complex model of Merlivat and Coantic (1975). We also examine the daily variation of leaf water composition using the model of Leaney et al. (1985).

## NOTATION

---

$b$	intercept of linear relationship between $\delta_2$ and $\delta_{18}$ of a compartment (eqn. (5))
$B$	diffusive fraction of transport resistance (eqn. (6))
$E$ ( $\text{mol m}^{-2} \text{s}^{-1}$ )	transpiration rate (eqn. (10))
$e^*$ (hPa)	saturation vapour pressure
$e^a$ (hPa)	vapour pressure in air (eqn. (1))
$e^{ef}$ (hPa)	vapour pressure of an evaporating front (eqn. (7))
$e^{lv}$ (hPa)	vapour pressure of leaf sub-stomatal cavity (eqn. (1))
$e^{sv}$ (hPa)	vapour pressure of soil evaporating front (eqn. (2))
$ET$	evapotranspiration
$f$	fraction of leaf water equilibrated with the atmosphere (eqn. (1))
$m$	slope of linear relationship between $\delta_2$ and $\delta_{18}$ of a compartment (eqn. (5))
MWL	meteoric water line, $m = 8$ , $b = 10$
$q$	characteristic of boundary layer; for static diffusion $q = 1$ , laminar flow $q = 2/3$ , and turbulent $q = 1/2$ (eqn. (6))
$r_M$	resistance due to molecular diffusion (eqn. (6))
$r_T$	resistance due to turbulent transport (eqn. (6))
$s$ (hPa $^{\circ}\text{C}^{-1}$ )	slope of sat. vapour pressure-temp. line
$T$ ( $^{\circ}\text{C}$ )	temperature
$x$	portion of $e^a$ derived from local surfaces (eqn. (3))
$y$	portion of $ET$ flux from leaves (eqn. (4))
$\delta$	isotope ratio as a delta value
$\delta_2$	delta value for $^2\text{H}/^1\text{H}$ in water
$\delta_{18}$	delta value for $^{18}\text{O}/^{16}\text{O}$ in water
$\delta^a, \delta^{a\infty}$	delta value of atmospheric water vapour; $a$ , near ground; $a\infty$ , above mixing layer (eqns. (1) and (3))
$\delta^{ef}, \delta^{efv}$	Delta value of: $ef$ , liquid and $efv$ , vapour at an evaporating front (eqns. (2), (7) and (9))
$\delta^{et}$	delta value of $ET$ vapour flux (eqn. (3))
$\delta^{in\phi}$	delta value of sap flowing into leaf (eqn. (1))
$\delta^{l\phi}$	delta value of vapour flux from leaf (eqn. (4))
$\delta^{lw}$	delta value of leaf water (eqn. (1))
$\delta^{s\phi}, \delta^{s\phi\infty}$	delta value of vapour flux from soil, and $sv\infty$ , steady-state value of same (eqns. (2) and (5))
$\delta^{liiss}$	delta value of liquid water in sub-stomatal cavity at steady-state (eqn. (11))
$\epsilon^*$	phase-change fractionation factor (eqn. (1))
$\tau$ (s)	turnover time of leaf water (eqn. (10))
$\Phi^W$ ( $\text{mol m}^{-2}$ )	leaf water content (eqn. (10))

---

## METHODS

A hand auger was used to obtain soil profiles. On bringing the soil to the surface, a subsample was collected in a 500-ml screw-cap jar which was sealed airtight with plastic electrical tape. Foliage samples were collected into 250-ml Quickfit® flasks, ~50 ml of Na-dried kerosene was added and the flasks were closed with a vacuum-greased ground-glass stopper. Around 5–8 g of foliage was collected, yielding 3–5 ml of water after distillation. The foliage samples were all taken from the mature, one-year-old portion of the canopy, since earlier studies had found consistently lower water compositions in the newly grown leaves, probably owing to the presence of petiole and green twig material (Walker and Brunel, unpublished observations, 1986–1988; see also Fig. 6).

The stem water was sampled from twigs and small branches 5–10 mm in diameter from which the bark had been removed quickly. These pieces of wood were stored in flasks as for the foliage. It was considered necessary to remove the bark surface which could absorb small amounts of, or exchange with, the water vapour in the atmosphere (Walker and Richardson, in preparation). Foliage, stem and soil water were recovered by distillation as described elsewhere (Walker et al. 1989).

Atmospheric water vapour samples were collected by pumping air through refrigerated traps, maintained at below  $-60^{\circ}\text{C}$ , at a flow rate of  $16\text{ l h}^{-1}$ . The traps had been demonstrated to be close to 100% efficient at water trapping under these conditions by operating a consecutive series of traps. Also, recovered  $\delta_2^a$  (see Notation for a definition of symbols) samples were similar in composition to samples concurrently trapped in dry ice–alcohol traps. The water vapour sampler was supplied by the Institut für Umweltphysik, Universität Heidelberg. Atmospheric water vapour was collected over intervals of 2–4 h, recovered samples (0.5–2.0 ml) were stored in small screw-cap vials sealed with tape. Air was sampled on a mast, with collection points at heights of 2.25, 4.5 and 9 m.

The  $\delta_2$  composition of water samples was estimated on a VG Micromass 602D mass spectrometer on  $\text{H}_2$  gas obtained by reducing a  $25\ \mu\text{l}$  water sample in a uranium oven. The  $\delta_{18}$  composition of water was estimated on a 3 ml aliquot by the Epstein–Mayeda  $\text{CO}_2\text{--H}_2\text{O}$  equilibration technique. Small volumes of water ( $\approx 0.1\text{ ml}$ ) were obtained from the atmosphere sampling. Their  $\delta_{18}$  compositions were analysed using a modification of the Epstein–Mayeda technique reported by Kishima and Sakai (1980) and modified further within our laboratory (Dighton, 1985). These techniques have standard deviations of 0.5‰ for  $\delta_2$ , 0.1‰ for  $\delta_{18}$ , and 0.5‰ for the small volume  $\delta_{18}$  analyses. Isotope compositions are relative to Vienna-Standard Mean Ocean Water and expressed in per mil (‰) units (Gonfiantini, 1984).

Transpiration rates were measured with a Licor® 1600 porometer. Foliage temperatures were measured using the porometer and with Everest® and Mikron® infra-red thermometers. Soil surface temperatures of sunlit, bare soil, shaded soil surface beneath trees and of the overall canopy from above were

obtained similarly. Humidity and air temperature measurements were kindly provided by J. Hartmann and F.X. Dunin, and W.R.N. Edwards kindly provided the ground cover data from aerial photographs of J. Hacker. The results were reported using local time (Australian Central Standard Time), which is around half an hour ahead of solar time.

#### STUDY AREA

The samples were collected from an area known as Hincks Conservation Park (33°53'S, 135°52'E) in mid-January and mid-March 1988. Annual rainfall in this area averages around 400 mm (Schwerdtfeger, 1985). Rainfall varies considerably between recording stations; however, there are broad indications of heavy falls of ~16 mm in early December, and 12 mm in late January. A number of other rains of ~1 mm were recorded. The annual deficit of rainfall below the potential evaporation is ~1600 mm (Jacobson and Lau, 1987). Light rain (0.5–1 mm) fell on three days during the March study. Meteorological studies performed concurrently with the sample collection found that the average daily maximum air temperature was 30°C over January 16–19 and 23.6°C over March 7–15, while relative humidity had average daily minima of 32.8 and 36%, respectively.

The vegetative cover was observed from aerial images to be around 24% *Eucalyptus* mallee and 45% of other, smaller vegetation (*Melaleuca* and *Triodia*); with 31% bare sand. The region consists of a series of parallel dunes, with the dune crests in a NE–SW direction across prevailing winds. A transect surveyed between the dune crests on either side of the experimental site found that these were ~900 m apart and reached an elevation of 5.5 m above the surrounding surface, with the experimental site roughly equidistant from either crest. The mallee were 2.3 m high on average, and the zero plane displacement was 1.8 m (Chen and Schwerdtfeger, 1989). The water table was estimated to be at a depth of at least 28 m.

#### THEORY

##### *Isotopic fractionation*

Two consecutive isotopic enrichments, or fractionations, are evident during evaporation, one is caused by the liquid–vapour phase change (known as the equilibrium fractionation effect) and the second takes place during vapour transport (kinetic fractionation effect). These processes have been described elsewhere (Craig and Gordon, 1965; Dongmann et al., 1974; Merlivat and Coantic, 1975; Welhan and Fritz, 1977; Farris and Strain, 1978; Bariac et al., 1983). Further refinements have been advanced by Leaney et al. (1985), Farquhar et al. (1987), Francey and Tans (1987) and Walker et al. (1989). These are all revisions of the principles advanced by Craig and Gordon (1965). The other workers consider non-steady-state enrichment, and where only a portion

of leaf water is fractionated (Bariac et al., 1983; Leaney et al., 1985). Walker et al. (1989) demonstrate that this portion varies with transpiration rate. The rate of approach to steady-state in the leaf is rapid (Leaney et al., 1985). Dongmann et al. (1974), Farris and Strain (1978) and Walker et al. (1989) examine the influence of turbulence on the kinetic fractionation, while Farquhar et al. (1987) adopt a notation emphasizing the fact that the kinetic fractionation is governed by the ratio of vapour pressures inside and outside the leaf ( $e^a/e^{lv}$ ), which we shall employ, rather than the related relative humidity.

In *foliage* we use a steady-state fractionation equation of the form

$$\frac{\delta^{lw} - \delta^{in\phi}}{f} = \varepsilon^* + \eta + \frac{e^a}{e^{lv}}(\delta^a - \delta^{in\phi} - \eta) \quad (1)$$

where:  $\delta$  is the isotopic composition and  $e$  the vapour pressure of a compartment, and the compartments are denoted by superscripts: lw = leaf water; in $\phi$  = the water entering the plant and flowing through the vascular system; lv = the water vapour in the substomatal cavity; a = atmospheric water vapour;  $\varepsilon^*$  is the equilibrium fractionation factor (Majoube, 1971);  $\eta$  is the diffusion ratio excess (Merlivat, 1978) and  $f$  is the fraction of the leaf water equilibrating with the atmosphere (Leaney et al., 1985; Walker et al., 1989). The  $e^{lv}$  is assumed to be saturated at leaf temperature, i.e.  $e^{lv} = e^*(T^l)$ . The convective influx of unfractionated water into a transpiring leaf mixes with fractionated water forming adjacent to the substomatal cavity, the site of the phase-change. If  $f = 1$ , eqn. (1) provides the steady-state composition of the water in the substomatal cavity,  $\delta^{tiss}$ , the liquid limit of  $\delta^{lw}$ . At steady-state, the composition of the water vapour flux from the leaf ( $\delta^{l\phi}$ ) is the same as the input, i.e.  $\delta^{l\phi} = \delta^{in\phi}$ .

The steady-state soil vapour flux composition is given by:

$$\delta^{s\phi\infty} = \frac{\delta^{ef} + \varepsilon^* + \eta + e^a/e^{sv}(\delta^a - \eta)}{(1 - e^a/e^{sv})} \quad (2)$$

where the principles remain the same as in eqn. (1), but the compartments have changed, as denoted by superscripts: sv = the water vapour in the soil; s $\phi$  = the composition of water vapour flux from the soil and s $\phi\infty$  is the same at steady state; ef = the liquid phase at the soil evaporating front.

At and below the evaporating front, the isotopic composition of soil vapour differs from the soil liquid composition by  $\varepsilon^*$  alone (Allison et al., 1987). Their data suggest that, at the evaporating front, the soil water vapour pressure is close to saturation, since little kinetic fractionation is apparent in vapours drawn from this region. We can expect an increase in the influence of kinetic fractionation in soil vapour from the evaporating front to the soil surface.

### *Evapotranspiration source model*

When atmospheric water vapour is sampled near the ground surface, it may be assumed to have a composition resulting from simple, fluid mixing of the

local water vapour fluxes ( $\delta^{et}$ ) with the water vapour initially present derived from above the mixing layer, high in the atmosphere ( $\delta^{a\infty}$ ) (Bariac et al., 1983), vis:

$$\delta^a = x\delta^{et} + (1 - x)\delta^{a\infty} \quad (3)$$

Moreover, the component due to evapotranspiration may be expressed in simple mixing terms relative to the proportions and composition of soil and plant water vapour, vis:

$$\delta^{et} = y\delta^{l\phi} + (1 - y)\delta^{s\phi} \quad (4)$$

Bariac et al. (1983) pointed out that the different compositions of these vapours may be used to partition the relative contributions from different sources. Their studies have only examined the  $\delta_{18}$  compositions of the various compartments (Bariac et al., 1983; Bariac et al., 1987), whereas in the current study, we also examine the  $\delta_2$  compositions. The linear inter-mixing model proposed should be verified by the compositions of the compartments plotting on straight ('mixing') lines on a graph of  $\delta_2$  against  $\delta_{18}$ , with the various sources located at the intercepts of such lines.

This model requires that any preferential accumulation of rain water by the tree (Fig. 1), will not create persistent lateral variations in the isotopic composition of soil water. Further, the different evaporating compartments may also be at different temperatures. Apart from the influence of temperature on ET rates, temperature also influences the magnitude of the equilibrium fractionation effect occurring at the phase change ( $\epsilon^*$ ) (Majoube, 1971). As a consequence, the composition of the total vapour flux to the atmosphere will be subject to variations in vapour compositions from evaporation sites in soil and foliage because of the daily cycles in their temperatures and the relative contributions from these sites over the course of the day. The model can be expected, therefore, to only apply to mean values obtained over intervals longer than a day or so.

#### *Influence of diffusion of 'mixing' lines*

Bariac et al. (1983) assume turbulent mixing of the various compartments. An alternative treatment considers the case where diffusive and turbulent transport occurs, using a number of boundary layer models (Merlivat and Coantic, 1975). These authors describe how  $\delta^a$  compositions over a theoretical evaporating front are distributed in a vertical gradient such that:

$$\delta_2^a = m\delta_{18}^a + b \quad (5)$$

Further, they demonstrate that the diffusive proportion of the total transport resistance,  $B$ , is:

$$B = qr_M/(r_M + r_T) \quad (6)$$

where:  $r_M$  is the resistance due to molecular diffusion,  $r_T$  is the resistance due

to turbulent transport, and  $q$  is a constant describing the characteristics of the boundary layer (see Notation). The diffusive proportion,  $B$ , may be calculated from the observed values of  $m$  and  $b$  in eqn. (5) above, and the composition of the vapour at the evaporating front,  $\delta^{\text{efv}}$ :

$$B = \frac{1}{1 - e^a/e^{\text{ef}}} \left( \frac{b - \delta_2^{\text{efv}} + m\delta_{18}^{\text{efv}}}{\eta_2 - m\eta_{18}} \right) \quad (7)$$

Rearranging, we see that  $\delta^{\text{efv}}$  is on a line parallel to the  $\delta^a$  line of eqn. (5), i.e.

$$\delta_2^{\text{efv}} = m\delta_{18}^{\text{efv}} + b + B(\eta_2 - m\eta_{18})(1 - e^a/e^{\text{ef}}) \quad (8)$$

The composition of vapour at the evaporating front may be calculated assuming saturated conditions, i.e.

$$\delta^{\text{efv}} = \delta^{\text{ef}} - \varepsilon^* \quad (9)$$

where the liquid composition ( $\delta^{\text{ef}}$ ) is measured directly.

The Merlivat-Coantic model differs from that of Bariac et al. (1983) in that the surface vapour values are not colinear with  $\delta^a$ , but are displaced to a parallel line. Further analysis may be made by considering specific values of  $B$ , which can vary between 0 and 1, corresponding to turbulence- or diffusion-

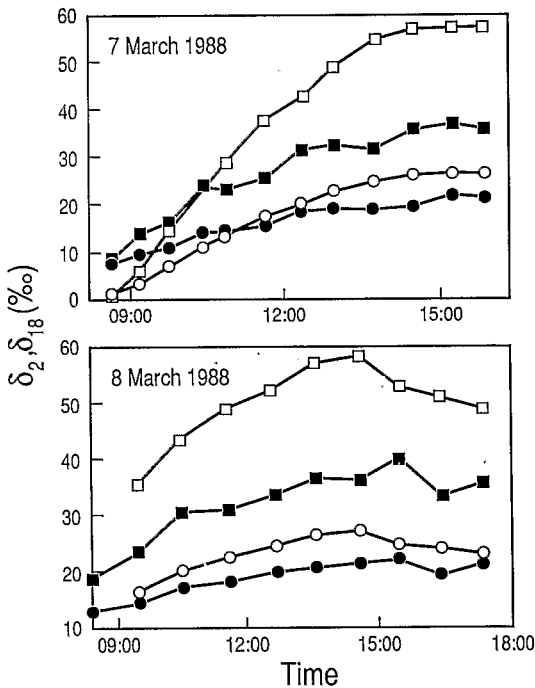


Fig. 2. Comparison of the theoretical steady-state (open symbols) and observed (filled symbols) of  $\delta_{18}$  (○) and  $\delta_2$  (□) compositions of *Eucalyptus* leaf water on 7 March and 8 March, 1988.



limited evaporation under wet or dry conditions respectively. Thus, the treatment of Bariac et al. (1983) corresponds to the case where  $B = 0$  in eqn. (8).

## RESULTS AND DISCUSSION

### *Foliage water*

The isotopic composition of foliar water ( $\delta^{lw}$ ) is in effective steady state with water in adjacent compartments (stem water,  $\delta^{in\phi}$ ; atmospheric water vapour,  $\delta^a$ ). This is demonstrated in two ways. Firstly, examination of  $\delta^{lw}$  in comparison with calculated steady-state compositions of the liquid water at the substomatal cavity ( $\delta^{tiss}$ ) shows similarly shaped curves (Fig. 2). The  $\delta^{tiss}$  values are based on the observed atmosphere vapour and stem water compositions and the meteorological conditions (Fig. 3), using the condition of  $f = 1$  in eqn. (1) as described earlier. The  $\delta^{lw}$  differ from the  $\delta^{tiss}$  values principally because only a

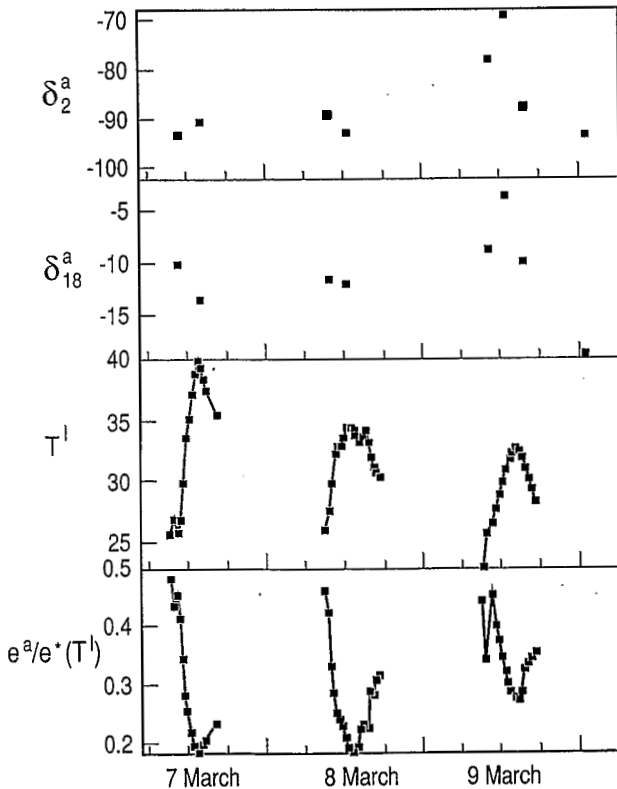


Fig. 3. Environmental parameters used in the calculation of steady-state compositions. The  $\delta^a$  compositions were linearly interpolated for values at the leaf sample times, the collection intervals of the atmosphere water vapour samples average around 2 h.

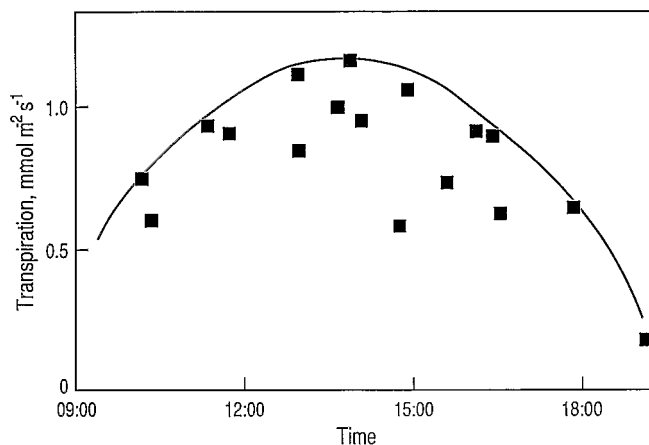


Fig. 4. Transpiration rates of *Eucalyptus* over several days (11–14 March 1988) of the study. Data are the means of six individual measurements.

fraction of the leaf water is in this equilibrated state, as was observed by Bariac et al. (1983) and modelled by Leaney et al. (1985) and Walker et al. (1989). However, the fact that the curve shapes of both actual  $\delta^{lw}$  and calculated  $\delta^{tiss}$  compositions are so similar suggests that the leaf water can be regarded as in steady-state for the duration of the day. Secondly, the transpiration rate,  $E$ , provides a measure of the turnover time for the leaf water. Figure 4 shows transpiration rates measured by porometry. At such rates, and with a water content,  $\Phi^W$ , of around  $9 \text{ mol m}^{-2}$ , the turnover time,  $\tau$ , is:

$$\tau = \Phi^W / E \quad (10)$$

which is around 2 h. These two exercises confirm that, viewed over a 24 h interval, water vapour derived from the leaves ( $\delta^{l\phi}$ ), must have the same composition as that entering it ( $\delta^{in\phi}$ ). This ignores the very minor quantities influenced by metabolic fractionations during water splitting in photosynthesis.

The fraction of leaf water equilibrated with the atmosphere,  $f$ , had a midday minimum (Fig. 5). The value of  $f$  is estimated by first calculating  $\delta^{tiss}$  as above and then writing:

$$f = (\delta^{lw} - \delta^{in\phi}) / (\delta^{tiss} - \delta^{in\phi}) \quad (11)$$

This suggests that there was a midday maximum in  $E$ , since there is an inverse relationship between  $f$  and  $E$  (Walker et al., 1989). Porometer measurements of  $E$  do indeed suggest such a maximum, as is quite normal (Fig. 4), although the two data sets were obtained on several different days, so only the general trends over a 24 h interval can be compared. Studies with heat pulse sap flow measurement also indicated a midday maximum (Walker and Edwards, in prep.). The estimation of  $E$  from  $f$  calculations on the basis of the earlier observations is premature, because of inter-species differences in leaf reticulation and resistance. However, the relatively high  $f$  values (Fig. 5) do suggest

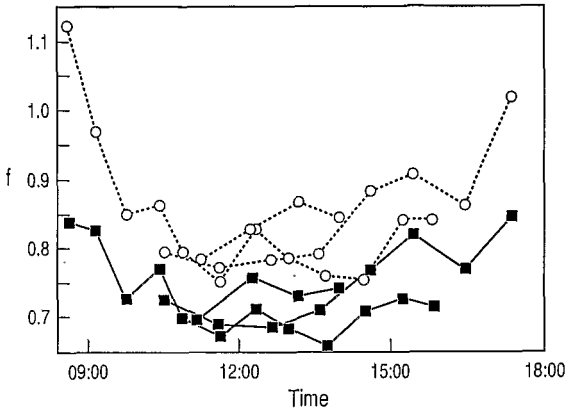


Fig. 5. Variation of the fraction of the leaf water equilibrated with the atmosphere over several days (7-9 March 1988) of the study. Estimates are based on  $\delta_2$  (■) or  $\delta_{18}$  (○). Data of different days are connected.

very low rates of  $E$ . An  $f$  value of 0.8 was observed in previous studies on wheat (Walker et al., 1989) to correspond to  $E \leq 0.7 \text{ mmol m}^{-2} \text{ s}^{-1}$ , which agrees well with the porometry measurements.

The composition of water from leaves of different ages was found to vary systematically in preliminary studies on 17 January (Fig. 6). The lower  $\delta^{18}\text{O}$  compositions observed in the younger, newly-emerging leaves can be attributed to the presence of petiole in addition to leaf blade material in these samples. The young petiole material was sampled because its green appearance

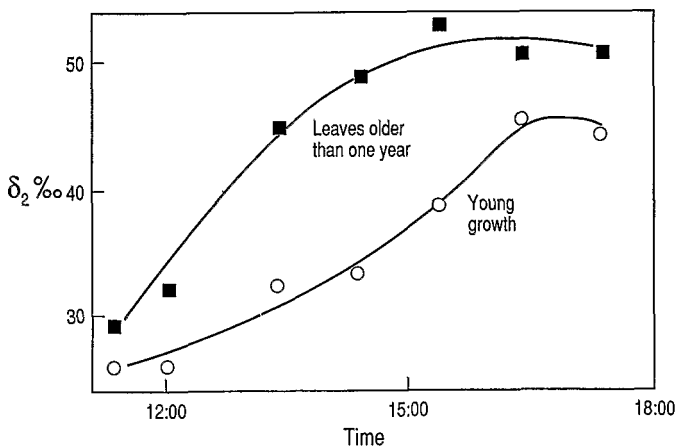


Fig. 6. The daily course of  $\delta_2$  composition of leaf water from newly growing leaves (○) and mature leaves (■) of *Eucalyptus* on 17 January 1988. Data are the means of duplicates.

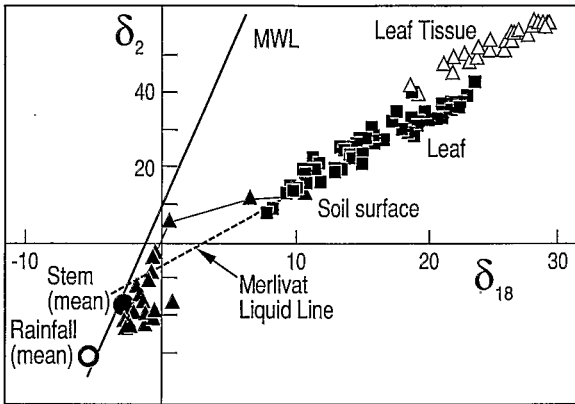


Fig. 7. The relationship between  $\delta_{18}$  and  $\delta_2$  of foliage (■), stem (●) and soil (▲) samples collected in March 1988. Long term precipitation mean for Adelaide is shown (○). Leaf tissue (△) are calculated leaf enrichments based on observed conditions and assuming  $f = 1$ .

suggested that it may be transpiring, i.e. fractionating, water. Different compositions in leaves of different age have been observed in previous studies (Walker et al., 1989).

The  $\delta$  values of the two isotopes were observed to be closely associated (Fig. 2). This behaviour occurs because the same physical fractionation processes are influencing both isotopes (Allison et al., 1985). Consequently, the isotope compositions plot in a linear locus when graphed against each other (Fig. 7).

The  $f$  value should in fact be the same for both isotopes. By inspection of eqn. (11), we note that  $\delta^{lw}$ ,  $\delta^{in\phi}$  and  $\delta^{tiss}$  will all be co-linear on a double isotope plot (such as Fig. 7) as a consequence of equality of  $f$  for  $\delta_2$  and  $\delta_{18}$  data. The observed  $f$  values computed for the different isotopes are higher for  $\delta_{18}$ , but show very similar trends between the two isotopes (Fig. 5). The consistent difference between  $f$  values (Fig. 5) is possibly because of the influence of turbulence on the kinetic fractionation (Walker et al., 1989), or minor errors in assessing environmental conditions which influence estimates of  $\epsilon^*$ ,  $e^a/e^{lv}$  and  $e^a/e^{sv}$ , affecting eqns. (1) and (2).

### Stem water

The extensive leaf composition data set confirms that the observed sap water composition is the input to the leaf tissue, since the mixing line is colinear with the stem water input (Fig. 7). Variations of  $e^a/e^{lv}$  and leaf temperature during the day result in slight changes in the relationship between  $\delta^{in\phi}$  and  $\delta^{tiss}$  (Allison et al., 1985), which will contribute some of the scatter of the  $\delta^{lw}$  data.

The stem water composition was very close to that of the soil at 0.3 m in January and around 0.7 m depth in March (Fig. 8). The change in composition of the sap water between January and March broadly matches that of the  $\delta$

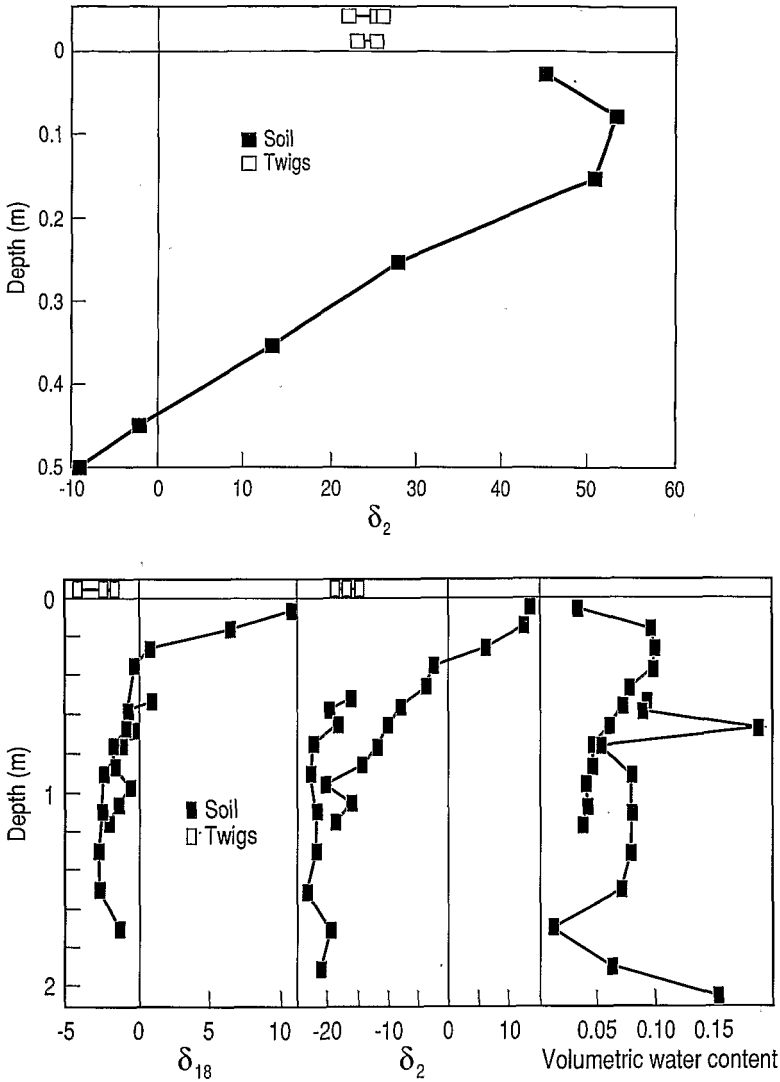


Fig. 8. Water content and isotopic compositions of soil water from two cores taken in (a) January and (b) March 1988. The mean stem water isotope compositions, with a horizontal bar to show the range of individual values, are indicated at the top of the soil profile.

values of the upper soil region. This need not imply that this water was taken up by the mallee at such depth. In fact, it is plausible that soil water at this depth is partly derived from root efflux. This suggestion is supported by the studies of Baker and van Bavel (1986), the 'hydraulic lift' concept of Richards and Caldwell (1987), and other evidence that water flow at the root-soil interface can be in a direction opposite to that usually assumed (reviewed by Kramer and Kozlowski, 1979; and Passioura, 1988). Further, the possible

isotopic equilibration (without a major net flux) of root water with adjacent soil water during passage up the root system must be considered. Cowan and Milthorpe (1968) advanced a model of water transport in the soil-plant-atmosphere that depicts a series of adjacent parallel pathways of discrete hydraulic resistances at different depths. As Passioura (1988) notes, there is still no physiological evidence of a 'non-return' valve to prevent water efflux, despite considerable speculation and interest in such an ability in plants. Consequently, the Cowan and Milthorpe model of hydraulic resistance as the control over water flux is remarkably acceptable over 20 years later. However, further evidence is needed to debate the quantitative importance of the processes mentioned.

### *Soil water*

The maximum  $\delta_2$  composition in the soil profile taken in January (Fig. 8a), is a little deeper than in March (Fig. 8b). This suggests that the evaporating front, which is associated with this maximum, is also deeper in the former. However, the depth of the evaporating front is generally fairly shallow. The January profile is also more enriched than that obtained in March, presumably as it had been longer since infiltration of rain into the profile. Hughes and Allison (1984) report long term estimates of average rainfall composition of  $\delta_{18} = -5.3\text{‰}$  and  $\delta_2 = -31\text{‰}$  for Adelaide. A similar value would be expected for this site and this point fits well for the composition at the bottom of the soil profile (Fig. 7).

A number of workers have estimated the evaporation rates of soils directly from isotope profiles (Barnes and Allison, 1988). This work has been undertaken on simpler, unvegetated systems (soil columns, dunes, lake beds) than we study here. Barnes and Allison (1988) discuss the characteristic time for the development of such an isotope profile, which is proportional to the reciprocal of the second power of the evaporation rate. The depth of the evaporating front is inversely proportional to the instantaneous evaporation rate. Although incompletely developed profiles have been modelled, it is acknowledged that there are difficulties in obtaining estimates of cumulative evaporation from such profiles (Walker et al., 1988). Thus we do not report analyses using these models.

Inspection of the isotope composition of water in the soil profiles (Fig. 8a, b) suggests that the March soil isotope profile was not fully developed, that the accumulation of isotopic excess due to evaporation had not proceeded to near steady-state conditions. This is a consequence of relatively recent infiltration of rain. We suggest from the shape of the isotope profile and the soil water content that there is an evaporating front in the shallowest, i.e. 0-100 mm, interval. Further, we expect that the composition of vapour leaving the soil surface is somewhat more depleted than the water entering this evaporating region from below, since the heavier isotopes are being left behind.

The steady-state composition of vapour leaving the soil surface ( $\delta^{s\phi\infty}$ ) was

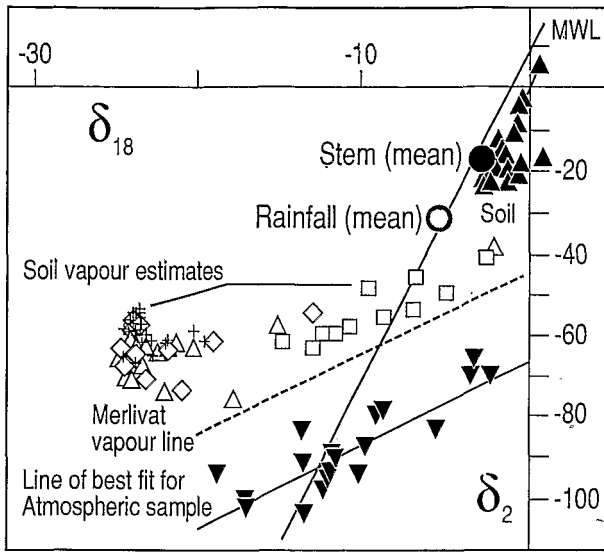


Fig.9. Theoretical  $\delta_{18}$  and  $\delta_2$  compositions of the soil vapour fluxes for different temperatures data sets ( $\square$ , canopy and soil from mast;  $+$ , bare sunlit soil;  $\Delta$ , shaded soil under canopy;  $\diamond$ , calculated temperature at 5 cm beneath shaded soil surface), the observed atmosphere compositions ( $\blacktriangledown$ ) and assumed foliage vapour flux (= stem composition,  $\bullet$ ) during the March study. The Merlivat vapour line is calculated with  $B = 1$  in eqn. (9), using the observed atmospheric vapour composition line and an average of  $e^a/e^{ef}$  of 0.15.

calculated (Fig. 9), given the composition at the evaporating front, specific humidity of the atmosphere, and the temperature of this soil region, using eqn. (2). The values are obtained using various soil temperatures (some shown in Fig. 10), and the  $\delta$  composition of the 0–100 mm interval for  $\delta^{ef}$  (Fig. 7). The  $\delta$  composition of the 0–100 mm interval will be slightly lower than  $\delta^{ef}$  since the sampled interval must include some soil above or below the evaporating front, which has the maximum enrichment (Barnes and Allison, 1988). Soil temperatures vary considerably between shaded and sunlit surfaces (sunlit temperatures not shown), and different values of  $\delta^{s\phi\infty}$  indicate the effect of this (Fig. 9). A similar effect may result if the evaporating front was some distance below the soil surface (Figs. 9 and 10). The estimated steady-state  $\delta_2^{s\phi\infty}$  values are considerably higher than the observed  $\delta_2^a$ , suggesting that the actual  $\delta_2^s$  composition is lower than  $\delta_2^{s\phi\infty}$ , as anticipated.

A further effect of temperature variation, over the daily cycle, is evident. The ground heat flux under shaded conditions reached around  $60 \text{ W m}^{-2}$ , indicating storage of around  $1.1 \text{ MJ m}^{-2}$  over the diurnal period (Fig. 10). Subsoil temperatures will be considerably higher than at the surface during a major portion of the nocturnal period, as this heat is released (De Vries and Philip, 1986). This can result in a water vapour pressure gradient near the surface which will drive upward vapour transport, with condensation on

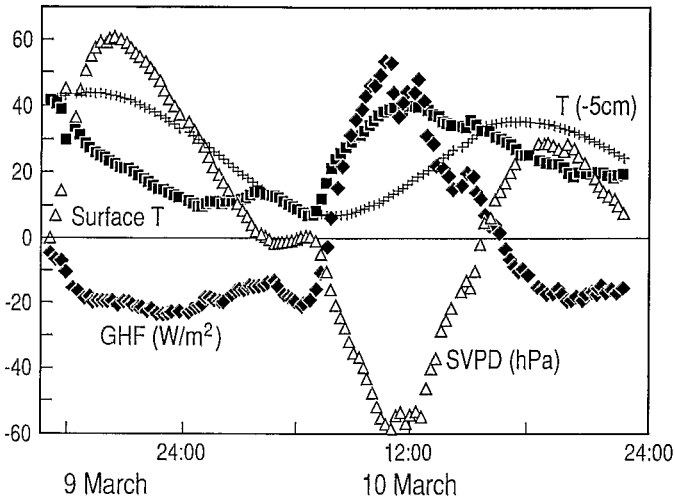


Fig.10. Temperature (■) and ground heat flux (◆) of shaded soil surface over 9–10 March; calculated estimates of the soil temperature at 5 cm depth (+); and saturation vapour pressure gradient between 5 cm and surface soil (△) under these conditions.

cooler, near-surface soil. Temperature differences over the top 0.05 m were up to 18°C, implying a saturation vapour pressure gradient of up to 60 hPa (Fig. 10). Measured depth profiles of temperature and vapour conductance in this soil would be required to accurately quantify such a two-step evaporation.

The vapour condensing in the subsoil during upward movement will be depleted in both isotopes in comparison to the soil liquid phase at the evaporating front. The condensates' isotopic composition will be to the left of the meteoric water line (MWL) shown in Fig. 9 (Fontes et al., 1978; Gat, 1980). Re-evaporation of the depleted condensate water would give rise to low  $\delta^{86}$  compositions in the early morning, and some evidence of this occurring was observed in  $\delta^a$  measurements (Figs. 3 and 9; some data not shown on a time basis). The atmospheric water vapour samples with low  $\delta_{18}$  compositions are a considerable distance from the MWL (Fig. 9), similar to the behaviour observed in other studies (Fontes et al., 1978; Gat, 1980) where a condensation step was involved in their generation.

#### *Atmospheric water vapour*

Atmosphere water vapour compositions are depleted compared with the other compartments sampled (soil, sap, foliage), as is commonly observed (Fig. 9). Generally,  $\delta^a$  values are observed to lie on the MWL ( $\delta_2^a = m\delta_{18}^a + b$ , where  $m = 8$  and  $b = 10$ , Yurtsever and Gat, 1981). The MWL is in fact derived from precipitation compositions. In this study, certain  $\delta^a$  measurements fell away from the MWL (Fig. 9), and there was a significantly different slope to the MWL



( $m = 8$ ) over all  $\delta^a$  data ( $m = 1.96$ , with a SE of 0.36; the regression is on 21  $\delta^a$  samples;  $r = 0.78$ ). This probably results from inputs to  $\delta^a$  which are not limited to the MWL slope. The similarity of the near-ground  $\delta^a$  compartment slope (Fig. 9) to those of the foliage and soil compartments (Fig. 7) suggests the influence of the latter two on the former. The mechanism involving soil condensation suggested earlier would cause a lower slope in the  $\delta^{sp}$  contribution to ET (Fontes *et al.*, 1978; Gat, 1980).

The variation of  $\delta^{sp}$  suggested earlier owing to two-stage evaporation may cause cycling of  $\delta^{et}$  because of the small size of a condensed vapour compartment at and near the soil surface. Temperature changes will also cycle  $\delta^{et}$ . Condensation on the soil surface will also occur nocturnally from the atmosphere, i.e. dewfall, as well as from the subsoil as suggested above. The cycling due to formation and evaporation of the condensate compartment would be along the  $\delta^a$  line observed in the data (Fig. 9). In this interpretation, the intersection of the  $\delta^a$  data line with the MWL is then the  $\delta^{a\infty}$  value, and  $\delta^a$  cycles either side of this, as a 'pulse' of soil and atmosphere water is 'pumped' up or adsorbed overnight and evaporates during the day.

This interpretation ignores the input of vapour from leaves, which is considerably different from the  $\delta^a$  in composition, as discussed earlier. If the  $\delta^a$  line indicates the variation in  $\delta^{et}$  as stated above, then one can calculate a corresponding  $\delta^{sp}$  line for the known  $\delta^{l\phi}$  and any given proportion of leaf vapour in the total ET flux ( $y$ , eqn. (3)). This  $\delta^{sp}$  line will be parallel to, and lie below, i.e. at more negative  $\delta_2$  values, the  $\delta^a$  line. The discussion of  $\delta^a$  compositions so far has only considered temperature effects and simple turbulent mixing in the Bariat model, and we will now consider the Merlivat-Coantic model.

The model of Merlivat and Coantic (1975) requires  $B$  to be able to estimate the line of surface vapour composition at the evaporating front, using eqn. (8). Under dry conditions, with the diffusion resistances of a dry soil layer and the stomata (stomatal resistances of 300–1500  $\text{sm}^{-1}$  were observed, data not shown),  $r_M \gg r_T$  and boundary layers will be fully diffusive, i.e.  $q$  approaches 1. Consequently,  $B$  will approach its maximum value of 1, see eqn. (7). If this is so, the mean  $\delta^{efv}$  composition lies on a 'Merlivat' line (Fig. 9) of:

$$\delta_2^{efv} = 1.96\delta_{18}^{efv} - 45$$

Thus, to cycle  $\delta^{et}$  on the  $\delta^a$  line, the vapour phase at a hypothetical evaporating front generating  $\delta^{et}$  would cycle on this line. This range of vapour compositions is possible with a single step evaporation from the soil  $\delta^{ef}$ . To demonstrate this, if we substitute for  $\delta_2^{efv}$  and  $\delta_{18}^{efv}$  using eqn. 9 in the vapour line above, we obtain the liquid composition of the evaporating front. At a nominal temperature of 30°C (Figs. 3 and 10), where  $\epsilon_2^* = 68.9$  and  $\epsilon_{18}^* = 8.9$ , this exercise yields:

$$\delta_2^{ef} = 1.96\delta_{18}^{ef} - 6.5$$

This liquid composition line is very close to the soil surface composition and also the lower values of the foliage (Fig. 7), supporting the earlier suggestion of the influence of these compartments on the  $\delta^a$  slope. Although the data does

support the suggested value of  $B$ , i.e. 1, further measurements are needed to verify that this is reasonable.

## CONCLUSIONS

The use of stable isotopes of water as natural tracers of soil-water movement in arid and semi-arid soil is well recognised (Barnes and Allison, 1988). The study of plant interactions in such systems has provided evidence of the similar enrichment of water in foliage to that observed in the soil. Because of the rapid equilibration of foliar water with that in the air and the incomplete nature of the enrichment, there remain difficulties in quantitative modelling of the transpiration and conductance of leaves purely on the basis of the isotopic composition of water. In the model of Leaney et al. (1985), only the rate of approach to the steady-state is influenced by transpiration rate, and this can be further influenced by changes in the relative water content (eqn. (2) of Leaney et al., 1985). Earlier studies (Dongmann et al., 1974; Farris and Strain, 1978) neglected the partial enrichment characteristic of leaves. Walker et al. (1989) found evidence that  $f$ , the fraction of leaf water equilibrated with the atmosphere, is modified by the transpiration rate. There is an inverse relationship between  $f$  and transpiration due to the increased convective influx of unfractionated sapwater into the leaf blade, diluting resident fractionated water adjacent to substomatal cavities. The same relationship was observed in the current study; midday  $f$  values were low while transpiration was high (Figs. 4 and 5).

The influence of vegetation on isotope profiles in soil is not clear. Allison and Hughes (1983) suggest that vapour transport of water to the root may occur in mallee under dry conditions, on the basis of observed enrichment of a soil profile at depth. Barnes and Allison (1988) have pointed out that temperature effects could give similar enrichment, and the present studies support this. It has also been observed that the peak of enriched water at the evaporating front of the soil is broader (Allison et al., 1983), possibly because of redistribution via the root system. However, the current study is limited by a lack of knowledge on the influence of vegetation on the introduction of newly fallen water to the soil profile. The infiltration of the soil by rain is undoubtedly aided to some extent by mallee root systems (Allison and Hughes, 1983). Although it is usually assumed that a soil profile is laterally homogeneous, the access to soilwater compartments of different isotopic composition within the rhizosphere, particularly in semi-arid environments, must be considered.

The influence of vegetation on atmospheric vapour composition in arid environments has received little attention. One striking characteristic of the current data is the similarity of the slopes of the atmospheric vapour and leaf liquid water  $\delta$  values, close to 2 in both cases (Figs. 7 and 9). This suggests that the two compartments are in equilibration and strongly interacting, exchanging water, if not necessarily resulting in a net flux of water. Therefore, it is remarkable that the  $\delta^a$  is considerably more depleted than the water efflux

from the leaves. However, this observation has been explained by showing that the soil evaporation can provide vapour of the appropriate composition.

The stable isotopes of water provide naturally occurring tracers that are used to study the hydrology of the unsaturated and saturated zones, particularly recharge and evaporation. The same techniques can provide insights into water movement in more complex environs, at the soil-plant-atmosphere interfaces (Salati et al., 1979; Bariac et al., 1987). In the current study, the  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$  were, respectively, enriched and depleted in comparison to the long term rainfall mean, which appears to be similar to the composition deep in the soil. These relative compositions suggest the non-steady-state stage of the ET flux from this environment. The calculated overall evaporating surface vapour line (Merlivat vapour line, Fig. 9) is also well below the long term rainfall mean, which is consistent with this conclusion. Such inter-relations may provide a means of understanding the hydrology of a plant-soil system. Since soil  $\delta$  values may never approach the accepted steady-state shape under vegetated conditions, because of the influence of the root systems, it may be important to further develop our understanding of the flux vapour relationships.

#### ACKNOWLEDGEMENTS

The support of research colleagues in providing data mentioned earlier and logistical support has been greatly appreciated. Technical support maintaining mass spectrometer facilities was received from J.C. Dighton.

#### REFERENCES

- Allison, G.B. and Hughes, M.S., 1983. The use of natural tracers as indicators of soil-water movement in a temperate semi-arid zone. *J. Hydrol.*, 60: 157-173.
- Allison, G.B., Barnes, C.J., Hughes, M.W. and Leaney, F.W.J., 1983. Effect of climate and vegetation on oxygen-18 and deuterium profiles in soils. In: *Isotope Hydrology 1983*. IAEA, Vienna, pp. 105-123.
- Allison, G.B., Gat, J.R. and Leaney, F.W.J., 1985. The relationship between deuterium and oxygen-18 delta values in leaf water. *Geochim Cosmochim. Acta*, 58: 145-156.
- Allison, G.B., Colin-Kaczala, C., Filly, A. and Fontes, J.Ch., 1987. Measurement of isotopic equilibrium between water, water vapour and soil  $\text{CO}_2$  in arid soil zones. *J. Hydrol.*, 95: 131-141.
- Baker, J.M. and van Bavel, C.H.M., 1986. Resistance of plant roots to water loss. *Agron. J.* 78: 641-644.
- Bariac, T., Ferhi, A., Jusserand, C. and Létolle, R., 1983. Sol-plante-atmosphère: contribution à l'étude de la composition isotopique de l'eau des différentes composantes de ce système. *Proc. Symp. Isotope Radn. Tech. Soil Phys. Irrig. Stud.* IAEA, Vienna, pp. 561-576.
- Bariac, T., Klamecki, A., Jusserand, C. and Létolle, R., 1987. Evolution de la composition isotopique de l'eau ( $^{18}\text{O}$ ) dans le continuum sol-plante-atmosphère (exemple d'une parcelle cultivée en blé, Versailles, France, Juin, 1984). *Catena*, 14: 55-72.
- Barnes, C.J. and Allison, G.B., 1988. Tracing of water movement in the unsaturated zone using stable isotopes of hydrogen and oxygen. *J. Hydrol.*, 100: 143-176.
- Chen, F. and Schwerdtfeger, P., 1989. Flux gradient relationships for momentum and heat over a rough natural surface. *Q. J. R. Meteorol. Soc.*, 115: 335-352.

- Cowan, I.R. and Milthorpe, F.L., 1968. Plant factors influencing the water status of plant tissues. In: T.T. Kozlowski (Editor), *Water Deficits and Plant Growth*, Vol. 1. Development, Growth and Measurement. Academic Press, New York, pp. 137-193.
- Craig, H. and Gordon, L.I., 1965. Deuterium and oxygen-18 variations in the ocean and the marine atmosphere. In: E. Tongiorgi (Editor), *Proc. Conf. on Stable Isotopes in Oceanographic Studies and Paleotemperatures*. Lab. Geol. Nucl., Pisa, pp. 9-130.
- De Vries, D.A. and Philip, J.R., 1986. Soil heat flux, thermal conductivity, and the null-alignment method. *Soil Sci. Soc. Am. J.*, 50: 12-18.
- Dighton, J.C., 1985. A method for the determination of the stable isotope composition ( $^{18}\text{O}$ ,  $^2\text{H}$ ) of small (< 25  $\mu\text{l}$ ) quantities of water. *Proc. 2nd Aust. Stable Isotope Conf.*, Macquarie University, 1985.
- Dongmann, G., Nürnberg, H.W., Förstel, H. and Wagener, K., 1974. On the enrichment of  $\text{H}_2^{18}\text{O}$  in the leaves of transpiring plants. *Radiat. Environ. Biophys.* 11: 41-52.
- Farquhar, G.D., Hubick, K.T., Condon, A.G. and Richards, R.A., 1987. Carbon isotope fractionation and plant water-use efficiency. In: P.W. Rundel, J.R. Ehlinger and K.A. Nagy (Editors), *Applications of Stable Isotope Ratios of Ecological Research*. Springer, New York, pp. 21-40.
- Farris, F. and Strain, B.R., 1978. The effects of water stress on leaf  $\text{H}_2^{18}\text{O}$  enrichment. *Radiat. Environ. Biophys.*, 15: 167-202.
- Fontes, J.Ch., Bortolami, G.C. and Zuppi, G.M., 1978. Hydrologie isotopique du massif du Mont-Blanc. *Proc. Symp. on Isotope Hydrology*, Neuherberg, 1978, Vol. I. IAEA, Vienna, pp. 411-440. Cited in: *Isotope Techniques in the Hydrogeological Assessment of Potential Sites for the Disposal of High-Level Radioactive Wastes*. IAEA, Vienna, 1983, pp. 51-54.
- Francey, R.J. and Tans, P.P., 1987. Latitudinal variation in oxygen-18 of atmospheric  $\text{CO}_2$ . *Nature (London)*, 327: 495-497.
- Gat, J.R., 1980. The isotopes of hydrogen and oxygen in precipitation. In: P. Fritz and J.Ch. Fontes (Editors), *Handbook of Environmental Isotope Geochemistry*. Elsevier, Amsterdam, pp. 21-47.
- Gonfiantini, R., 1984. Advisory group meeting on stable isotope reference samples for geochemical and hydrological investigations. IAEA, Vienna.
- Hughes, M.W. and Allison, G.B., 1984. Deuterium and oxygen 18 in Australian rainfall. *Tech. Pap. No. 46*, CSIRO Div. Soils, CSIRO, Melbourne.
- Jacobson, G. and Lau, J.E., 1987. *Hydrogeology of Australia*. G.W. D'Addario (Editor), Mercury-Walch, Hobart.
- Kishima, N. and Sakai, H., 1980. Oxygen-18 and deuterium determination on a single water sample of a few milligrams. *Anal. Chem.*, 52: 356-358.
- Kramer, P.J. and Kozlowski, T.T., 1979. *Physiology of Woody Plants*. Academic Press, New York, p. 471.
- Leaney, F.W., Osmond, C.B., Allison, G.B. and Ziegler, H., 1985. Hydrogen-isotope composition of leaf water in C3 and C4 plants: its relationship to the hydrogen-isotope composition of dry matter. *Planta*, 164: 215-220.
- Majoube, M., 1971. Fractionnement en oxygène-18 et en deuterium entre l'eau et sa vapeur. *J. Chim. Phys.*, 68: 1423-1436.
- Merlivat, L., 1978. Molecular diffusivities of  $\text{H}_2^{16}\text{O}$ ,  $\text{HD}^{16}\text{O}$ , and  $\text{H}_2^{18}\text{O}$  in gases. *J. Chem. Phys.*, 69: 2864-2871.
- Merlivat, L. and Coantic, M., 1975. Study of mass transfer at the air-water interface by an isotopic method. *J. Geophys. Res.*, 80: 3455-3464.
- Passioura, J.B., 1988. Water transport in and to roots. *Annu. Rev. Plant Physiol. Plant Mol. Biol.*, 39: 245-265.
- Richards, J.H. and Caldwell, M.M., 1987. Hydraulic lift: substantial nocturnal water transport between soil layers by *Artemisia tridentata* roots. *Oecologia*, 73: 486-489.
- Salati, E., Dall'Olio, A., Matsui, E. and Gat, J.R., 1979. Recycling of water in the Amazon basin: An isotopic study. *Water Resour. Res.*, 15: 1250-1258.
- Schwerdtfeger, P., 1985. Climate. In: C.R. Twidale, M.J. Tyler and M. Davies (Editors), *Natural History of Eyre Peninsula*. R. Soc. South Aust., Adelaide, pp. 89-100.

- Walker, C.D. and Richardson, S.B., 1990. The use of stable isotopes of water in characterising vegetation water sources. *Chem. Geol.*, in preparation.
- Walker, G.R., Hughes, M.W., Allison, G.B. and Barnes, C.J., 1988. The movement of isotopes of water during evaporation from a bare soil surface. *J. Hydrol.*, 97: 181-197.
- Walker, C.D., Leaney, F.W., Dighton, J.C. and Allison, G.B., 1989. The influence of transpiration on the equilibration of leaf water with atmospheric water vapour. *Plant Cell Environ.*, 12: 221-234.
- Welhan, J.A. and Fritz, P., 1977. Evaporation pan behaviour as an index of isotopic evaporation conditions. *Geochim. Cosmochim. Acta*, 41: 682-686.
- White, J.W.C., 1983. The climatic significance of D/H ratios in White Pine in the northeastern United States. Ph. D. Thesis, Columbia University, New York.
- Yurtsever, Y. and Gat, J.R., 1981. Atmospheric waters. *In: J.R. Gat and R. Gonfiantini (Editors), Stable Isotope Hydrology. Deuterium and Oxygen 18 in the Water Cycle.* IAEA Tech. Rep. No. 210, IAEA, Vienna.
- Zundel, G., Miekley, W., Grisi, B.M. and Förstel, H., 1978. The  $H_2^{18}O$  enrichment in the leaf water of tropic trees: Comparison of species from the tropical rain forest and the semi-arid region of Brazil. *Radiat. Environ. Biophys.*, 15: 203-212.