

Stable isotopes in soil and water studies

Isotopes stables dans l'eau et le sol

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ABSTRACT – The composition of oxygen-18 and deuterium in soil waters varies mainly as a result of changes in the isotopic composition of rainfall and the processes of evaporation. This paper gives examples of how the isotope profiles which develop in the unsaturated zone can give information about recharge fluxes and mechanisms, evaporation from groundwater systems in arid areas and the zones in soil profiles from which plants use water. J.-Ch Fontes and his colleagues have been leaders in the application of these techniques to the measurement of evaporation from deep water tables in arid areas.

Keywords: deuterium, oxygen-18, arid zones, unsaturated zone, ground-water, soils.

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RÉSUMÉ – La distribution de l'oxygène 18 et du deutérium dans les eaux souterraines varie essentiellement en raison des variations de la composition isotopique des eaux météoriques et des processus d'évaporation. Des exemples d'études de profils isotopiques dans la zone non saturée sont présentés. Ils informent sur les mécanismes et taux de recharge, l'évaporation à partir des aquifères profonds dans les zones arides et les profils de sols approvisionnant les plantes en eau. Jean-Charles Fontes et ses collaborateurs ont été des leaders dans les domaine des mesures d'évaporation à partir des aquifères profonds dans les zones arides.

Mots clés : deutérium, oxygène-18, zones arides, zones non saturées, eaux souterraines, sols.

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BACKGROUND

In the 1960s much work was done on the isotopic behaviour of precipitation and water evaporating from open water bodies.

In the late sixties, Zimmermann *et al.* (1967) started work on the behaviour of isotopes in porous materials and showed that when saturated sands were subject to evaporation the isotopic composition of the water decreased exponentially (both oxygen-18 and deuterium) from a maximum at the surface. This work was extended to unsaturated zone by Munnich *et al.* (1980) and Allison (1982).

In the early 1980s Fontes and his students started work on changes in the isotopic composition of soil water in deep unsaturated zones in the Sahara. At the same time, Allison and Barnes were investigating the behaviour of isotopes in the laboratory and in simple field systems. At this time, the French and Australian workers were not aware of each others work, however, after some very interesting field profiles were obtained by Fontes and his students and initial theoretical work had been carried out by Barnes and Allison, the two teams started to work together in late 1983.

Barnes and Allison (1988) reviewed work on the behaviour of isotopes in the unsaturated zone.

INTRODUCTION

The symbols used are defined in the Notation section.

Following Zimmermann *et al.* (1967) it can be shown that for saturated soils:

$$\delta = \delta_{\text{res}} + (\delta_{\text{o}} - \delta_{\text{res}}) \exp(-z / z_1)$$

$$\text{where } z_1 = D_l^* / E$$

In unsaturated soils, either evaporating under steady state conditions with the water table at depth, or evaporating under non-steady conditions, water vapour is lost from a region known as the evaporating front which is well defined in light textured soils, but may be more diffuse in soils of higher clay content.

Beneath the evaporating front, water and isotope movement is mainly in the liquid phase, while above it, vapour transport dominates. For this reason, the isotope profile, beneath the evaporating front, at least under isothermal conditions, appears to be similar in shape but not in detail to that observed in saturated soils. In this case Barnes and Allison (1983) showed that:

$$\delta = \delta_{\text{res}} + (\delta_{\text{ef}} - \delta_{\text{res}}) \exp \left[- \int_{z_{\text{ef}}}^z dz / (z_1 + z_v) \right]$$

$$\text{where } z_v = \alpha^* \sigma^v D_v^* N_{\text{sat}} / E \rho$$

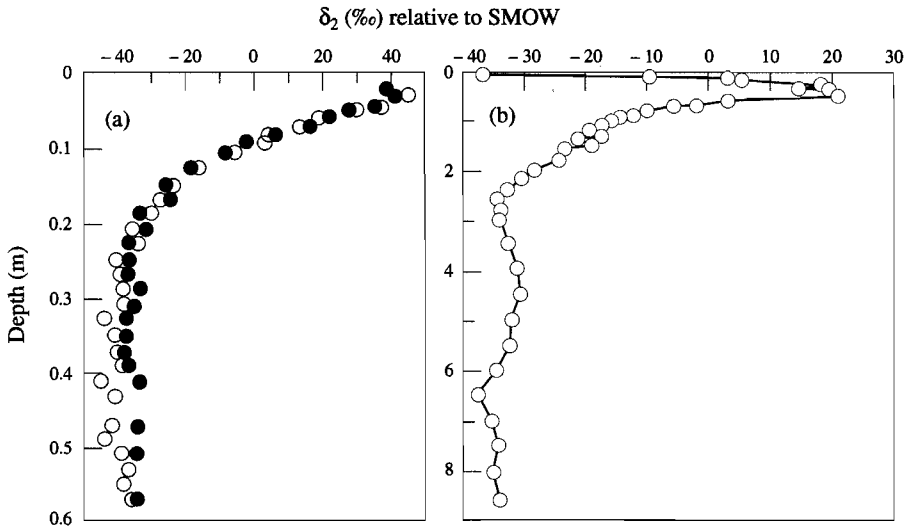


FIGURE 1.

Deuterium profiles for unsaturated soils undergoing evaporation (a) under steady state in the laboratory (from Allison *et al.*, 1983a), (b) from an arid zone dune (from Barnes and Allison, 1982).

Profils du deutérium en sols non saturés sous évaporation (a) en régime stationnaire au laboratoire (Allison et al., 1983a), (b) d'une dune en zone aride (Barnes et Allison, 1982).

As the effective liquid and vapour diffusivities (D_l^* , D_v^*) are controlled by a number of factors including the water content, this equation suggests that as the water content becomes lower beneath the evaporating front, the isotope profile will penetrate deeper into the soil. The magnitude of δ_{ef} is determined not only by processes in the soil, but also by the isotopic composition of atmospheric water vapour, the relative humidity of the air, as well as the diffusivity of water vapour and isotopes above the evaporating front.

Figure 1a shows typical isotope profiles for water evaporating under steady state conditions in the laboratory, while Figure 1b shows a profile from an arid zone dune.

One of the significant differences between evaporation from a saturated surface (either free water or a saturated soil) and a surface where evaporation proceeds through a dry layer is the slope of the deuterium- ^{18}O relationship.

When evaporation takes place two types of fractionation give rise to enrichment of isotopes at the evaporating surface. These are:

- the equilibrium effect due to small differences in the chemical potential between the isotopic species. This effect for HD^{16}O is about eight times that for H_2^{18}O .

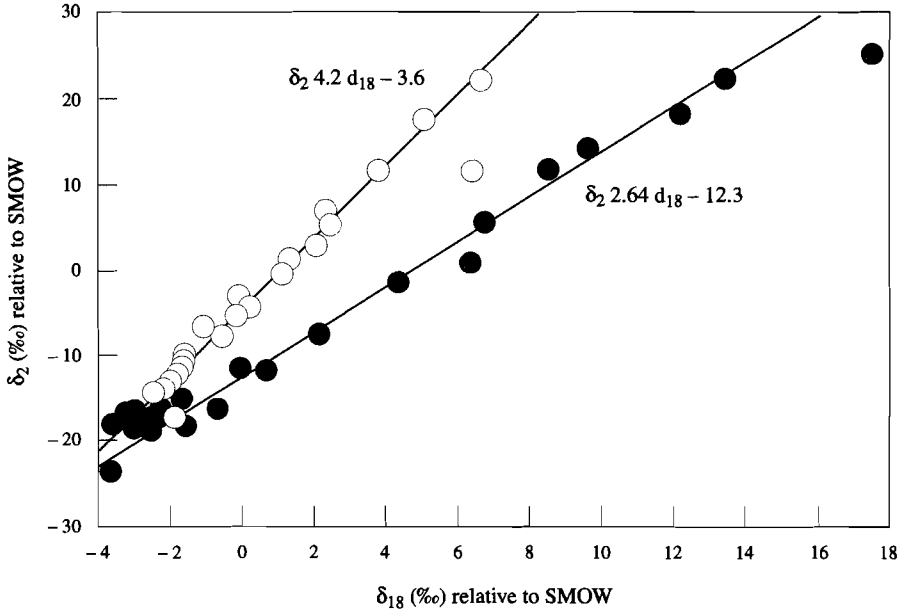


FIGURE 2.

Oxygen-18 deuterium relationships for laboratory columns undergoing steady state evaporation. The upper regression is for saturated and the lower for unsaturated conditions (from Barnes and Allison, 1988).

Relations ^{18}O -deutérium en colonnes de laboratoire sous évaporation en régime stationnaire. La droite de régression supérieure correspond aux conditions de saturation ; la droite inférieure aux conditions non saturées (Barnes et Allison, 1988).

- the kinetic effect due to different rates of diffusion of the isotopic species in the vapour phase. In this case both isotopic species behave in a similar fashion, Merlivat (1978).

As the evaporating front moves further into the soil profile the relative importance of the kinetic effect increases because of the development of a superficial dry layer where diffusive transport of water vapour dominates, leading to a reduction in the slope of the deuterium- ^{18}O relationship (Allison *et al.* 1983a). This is shown in Figure 2.

As evaporation in field soils always occurs under non-isothermal conditions it is important to assess the impact of temperature profiles on isotope profiles.

Using what they assumed were appropriate temperature gradients, Barnes and Allison (1984) showed that the effect of temperature on the isotope profiles was reasonably small but could explain a secondary minimum in the profile which is often observed in field situations. Theoretical profiles are shown in

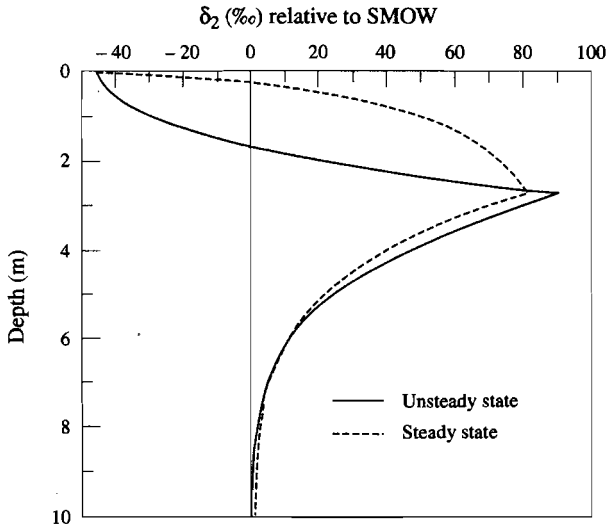


FIGURE 4.

A comparison of theoretical steady state and non-steady state deuterium profiles for the same instantaneous rate of evaporation (from Barnes and Walker, 1989).

Comparaison des profils du deutérium en régimes théoriques stationnaire et non stationnaire pour un même taux instantané d'évaporation (Barnes et Walker, 1989).

come this difficulty Shurbaji and Phillips (1995) published recently details of a numerical model for water, isotopes and heat transport in the unsaturated zone.

Barnes and Walker (1989) showed, for what they believe to be conditions representative of evaporation in the field, that a major difference in steady state and non-steady state conditions is in the shape of the profile above the evaporating front as shown in Figure 4.

The above discussion is directed mainly at the changes in isotopic composition which occur as a result of evaporation from the soil surface. This is one of the major driving forces which brings about changes in the isotope concentrations in the unsaturated zone. However, changes in the isotopic composition can also be brought about by infiltration of rainfall of different composition or condensation or partial freezing of soil water.

Stable isotopes at environmental concentrations in the unsaturated zone have been used to obtain information about several aspects of the hydrologic cycle namely:

- groundwater recharge
- processes by which infiltration occurs
- rates of evaporation from soils and shallow groundwater systems
- depths of water uptake by vegetation

GROUNDWATER RECHARGE

In using concentrations of stable isotopes to study groundwater recharge, piston flow where inputs are layered, but with mixing by diffusion, has been found to be a useful model in the unsaturated zone. However, in some studies much has been learned about flow in macropores or other structures from the study of stable isotopes in the unsaturated zone.

As a general rule stable isotopes have been most successful in recharge studies when the recharge fluxes are relatively high, say 200 mm per year or greater. It is also necessary for there to be seasonal changes in the isotopic composition of rainfall. This makes the technique most applicable for cool humid areas where there is a significant difference in the isotopic composition of summer and winter precipitation.

In principle however, the technique could be used in tropical areas provided there is a seasonal dry period where a significant isotope enrichment profile could develop as a result of evaporation and that this could then be displaced into the soil profile as a result of subsequent rainfall thus giving an annual signal which could then be observed during soil sampling.

It has been found that vegetation has little impact on concentrations of stable isotopes in soil water ; however, to obtain reliable estimates of recharge, soil samples for determining isotope concentrations should be taken from beneath the zone where extraction by roots is occurring.

Several authors have used this approach successfully, e.g. Thoma *et al.* (1979) and Saxena and Dressie (1983). Best estimates are obtained when long cores of the unsaturated zone are taken. This enables several years recharge to be reflected in the isotope profile (see for example Figure 5). In this case the higher the recharge rate the better will be the precision of estimates of recharge.

Allison *et al.* (1983b) showed that in areas of limited vegetation and low rates of recharge it was possible to show that there was a linear relationship between the shift in isotopic composition from the meteoric water line and the inverse of the square root of recharge. From limited field data there was agreement with this relationship ; however, this approach has not been tested further and, if useful, will only be appropriate for very low rates of recharge (less than 10 mm per year) in areas where transpiration is relatively unimportant.

PROCESSES BY WHICH INFILTRATION OCCURS

Fontes (1983) showed that a range of processes can occur during infiltration and the interaction between water in small and large pores may be especially complex. Much of this work was carried out in lysimeters. There

behaviour at low water contents and there may be problems in determining this.

- Use of the position of the maximum in the isotope profile to determine the depth of the evaporating front and then use this depth combined with the diffusivity of water vapour to obtain an estimate of evaporation rate. This technique is best for low rates of evaporation.
- Use of the shape of the isotope profile in the region above the evaporating front; however, this is not likely to be successful often, as there are sampling and analytical problems associated with the very low water contents usually encountered in this region.

A good example of the use of these techniques on field data is given in Fontes et al (1985) who studied steady state evaporation from a water table at greater than 10 metres depth in the Sahara. Their oxygen-18 profile is shown in Fig. 7. Note the similarity in shape to Fig 1a. In this study the first two

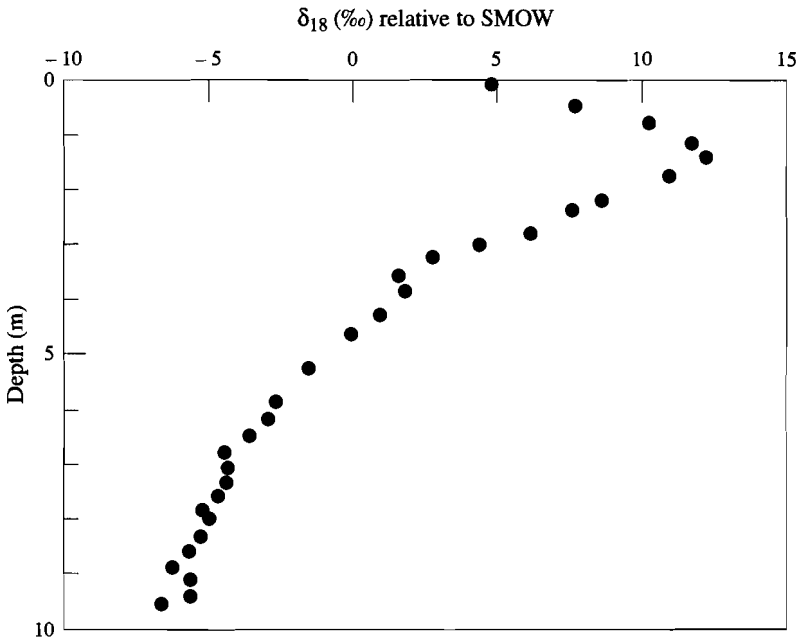


FIGURE 7.

The oxygen-18 profile for steady state evaporation from a water table at depth (from Fontes et al., 1986)

Profil ^{18}O sous évaporation en régime stationnaire d'une nappe d'eau en profondeur (Fontes et al., 1986).

methods above were used to obtain estimates of long term evaporation rate which are essentially independent. There were 2.2 and 1.4 mm a⁻¹. Although not in close agreement the match is reasonable in light of the difficulty of estimating the tortuosity of liquid water in these dry soils. The techniques used are probably the only ones available to estimate low rates of evaporation. Fontes and his colleagues (Aranyossy *et al.*, 1992) extended this work to estimate evaporation from water tables at various depths in an arid region of Niger.

Christmann and Sonntag (1987) also studied evaporation from deep sandy soils in hyper-arid regions in the Sahara and estimates of evaporation rate were made on the basis of steady-state conditions.

For steady-state evaporation from water tables several meters beneath the soil surface, long times (decades to centuries) may be needed to establish steady-state isotope profiles. For this reason the techniques discussed here will be useful only in very arid areas. However as shown in Fontes *et al.* the isotope profiles can be used to find the position of the evaporation front and hence the instantaneous evaporative flux using the second method above.

As discussed earlier, the secondary minimum which occurs in some profiles can in part be explained by temperature gradients in the unsaturated zone. However, temperature does not seem to play a major role in field profiles although a large number of sites show similar characteristics with a secondary minimum beneath a region where there is exponential-like decay beneath the evaporating front. The secondary minimum seems to be more extensive than can be explained by temperature gradients as shown in Figure 8.

In the field, especially in more temperate areas, profiles rarely reach steady state unless the water table is quite near the surface. However, in more arid areas, if rainfall does not penetrate to significant depth, this may be all lost by evaporation without disrupting the isotope profile. This is likely to be the case in the profiles investigated by Fontes *et al.* (1985).

Barnes and Walker (1989) showed that the exponential part of the profile beneath the evaporating front could give a reasonable estimate of the instantaneous evaporation rate from a soil where evaporation was proceeding under non-steady state conditions.

In arid zones where estimates of evaporation from water tables at depth are often remote, sampling equipment is often difficult and expensive to position. For this reason Fontes and colleagues attempted the use of samples of soil CO₂ and water vapour for determining ¹⁸O and deuterium profiles in soil water (Allison *et al.* 1987). In their preliminary work they were able to obtain reasonable agreement between δ_2 and δ_{18} for actual soil water samples and those in water vapour and CO₂ in the soil after correction for fractionation factors. However their samples were collected at atmospheric pressure and

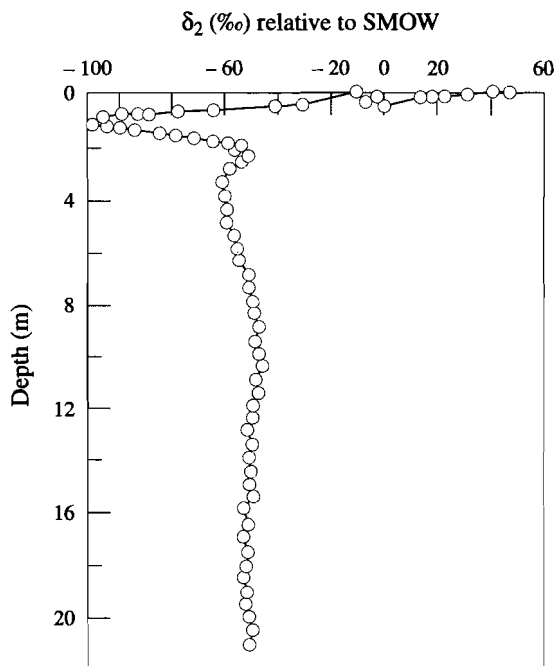


FIGURE 8.

The depth profile of deuterium for an arid zone dune (from Barnes and Allison, 1988).

Profil du deutérium en fonction de la profondeur pour une dune en zone aride (Barnes et Allison, 1988).

problems with condensation of the water vapour and re-equilibration with CO_2 is likely to have introduced errors in the δ_{18} values.

If this technique can be proven to be adequate it has the advantage that less field equipment is needed. A simple, small diameter spike is driven to the required depths and samples withdrawn. The use of this technique has been followed up by Amundson and Wang (1995) who used a similar technique but overcame problems of condensation by drying the samples of soil gas. Their data also suggested that soil CO_2 was in equilibrium with soil water.

Diffuse discharge is often an important component of the water balance of groundwater systems – for example the aquifers beneath the Sahara and the Great Artesian Basin (GAB). Such discharge may be an important component of the water balance and may need to be evaluated to estimate the sustainable yield of some groundwater systems.

For example, Woods (1990) used the techniques described here to show that diffuse discharge from a part of the GAB was approximately four times that from springs which were the generally accepted outflow points of this aquifer.

WATER UPTAKE BY PLANTS

White *et al.* (1985) was able to partition water being used by plants as coming from groundwater or soilwater or a combination of both. Since this work, a number of studies aimed at determining the depth in the soil from which water is extracted.

It has now been well documented that with few exceptions water uptake by vegetation is non-fractionating and that the isotopic composition of water in small twigs is representative of that extracted by roots.

Dawson and Ehleringer (1991) used deuterium values to determine the water uptake patterns of riverbank vegetation, and showed that small trees and shrubs extracted water which had a similar isotopic composition to that of a nearby stream. The interesting result found in this study was that the larger trees did not seem to be drawing water from the same source even though it was freely available.

A rather similar result was found by Thornburn and Walker (1994) who showed that mature Eucalyptus trees took up soil water from depth rather than water which had infiltrated into the surface soil as a result of flooding even though the inundation lasted for several months. Both these data and those above have shown that at least for mature vegetation the source of soil water is not necessarily related to the availability of water.

There can be significant changes in the isotopic composition of soil water with depth as a result of different rainfall events, evaporation, groundwater inflow or bank storage. However, in many actual soil profiles it is not possible to assign unambiguously, using ^{18}O or deuterium values, the depths from which uptake occurs. Brunel *et al.* (1995) used matric and osmotic potentials together with isotopes to partition which of two or three soil compartments vegetation was drawing water from. As simple techniques are now available for estimating matric potentials in soils, this seems a promising approach.

Stable isotopes provide possibly the only way to determine the source of water used by vegetation in field environments and it is likely that literature in this field will continue to grow.

CONCLUSIONS

The study of the behaviour of stable isotopes in the unsaturated zone has been taking place over the past three decades. Only limited advances have been made in the development of new theory or applications for studying recharge or evaporation in the last decade; however, significant advances have been made in this time in evaluating the sources of water used by vegetation.

In the future, stable isotopes are likely to be an important tool for studying regions of very low recharge. They are likely to be particularly important in

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Notation

D_l^*	Effective liquid diffusivity of isotopes
D_v^*	Effective diffusivity of water vapour
E	Evaporation rate
N_{sat}	Saturated water vapour density
z	Depth coordinate, positive downwards
z_{ef}	Depth of evaporating front
z_l	Length scale for liquid diffusion
z_v	Length scale for vapour diffusion
α^*	Equilibrium fractionation factor
δ	Isotope ratio delta-value
δ_{res}	Delta value of feed water
δ_{ef}	Delta value at $z = z_{\text{ef}}$
δ_0	Delta value at the surface
δ_2	Delta values for $^2\text{H}/^1\text{H}$ ratios
δ_{18}	Delta values for $^{18}\text{O}/^{16}\text{O}$ ratios
σ_v	kinetic fractionation factor
ρ	Density of liquid water
‰	Parts per thousand