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Thierry Bariac, Pascale Maillard, Jean-Marc Bonnefond. Contributing of isotope methodology to the analysis of water transfer in the soil-plant-atmosphere continuum. Actes de l'Ecole chercheurs INRA en Bioclimatologie, le Croisic, 3-7 avril 1995. Tome 1 : De la plante au couvert végétal. Editeur : Institut National de la Recherche Agronomique. 670 p., 1996, 10.13140/RG.2.1.3568.3688 . hal-02965627

**HAL Id: hal-02965627**

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Bariac T., Maillard P., Bonnefond J.M., 1996. Apports de la méthodologie isotopique à l'analyse du transfert de l'eau dans le continuum sol-plante-atmosphère. *In* : Actes de l'Ecole Chercheurs INRA en Bioclimatologie, Le Croisic, 3 - 7 avril 1995. Tome 1 : De la plante au couvert végétal. Organized by Pierre Cruiziat & Jean-Pierre Lagouarde. Editor : INRA, Département de Bioclimatologie, Thiverval-Grignon F78850 France. 593-615. ISBN-10 : 2-7380-0662-0 (ISBN-13 : 978-2-7380-0662-2).

## **Contributing of isotope methodology to the analysis of water transfer in the soil-plant-atmosphere continuum**

Thierry Bariac<sup>1</sup>, Pascale Maillard<sup>2</sup>, Jean-Marc Bonnefond<sup>3</sup>

<sup>1</sup> Laboratoire de Biogéochimie Isotopique U.P.M.C. – INRA, UMR 162, CNRS, Case 120, Place Jussieu, 75252 Paris cedex

<sup>2</sup> UA de Bioclimatologie-IAF, INRA, Domaine de Crouelle, 63039 Clermont-Ferrand cedex 02

<sup>3</sup> Station de Bioclimatologie, INRA, BP81, 33883 Villenave d'Ornon

**Key words:** oxygen-18, deuterium, water, soil-plant-atmosphere, transpiration, evaporation, leaf, collar

### **1. INTRODUCTION**

The work, presented briefly below, is for understanding and assessing the fate of different isotopes of water in the soil-plant-atmosphere.

Taking into account these intrinsic markers of the water molecule can supplement or refine the water balance in the compartments of the soil-plant-atmosphere continuum.

The isotopic approach can, in particular, help to determine the origin of the water that supplies reservoirs of interest and interpret or reconstruct the history of this water in these reservoirs.

### **2. REMINDERS ON THE THEORY**

#### **2.1. Isotopic ratio, $\delta$ unit, isotopic fractionation factor, isotopic enrichment factor**

These considerations refer only to heavy stable isotopes (oxygen-18 or <sup>18</sup>O; deuterium or <sup>2</sup>H) whose concentration varies only marginally in natural environments (<sup>18</sup>O: 0.204%, <sup>2</sup>H: 0.015%) compared to light isotopes of water (<sup>16</sup>O: 99.759%, <sup>1</sup>H: 99.985%).

Slight variations of these concentrations have imposed the development of very accurate isotopic analyses. At the beginning of analytical developments, the isotopic composition of water in a sample was expressed as a ratio: <sup>18</sup>O/<sup>16</sup>O or <sup>2</sup>H/<sup>1</sup>H. Then, researchers discovered that the measure of the isotopic ratio given by the mass spectrometer was very precise on a short term, but on a long term the accuracy of the data were of poor quality and did not ensure good reproducibility of long-term measures. However, if a sample is systematically compared to the same sample playing the role of reference ("standard"), the difference observed between sample and reference will remain constant over time. Then, instrumental fluctuations, which affect the correctness of the determination of the

absolute isotopic composition, will affect the isotopic ratio of the sample in the same way as that of the reference. This will offer a better reproducibility of the measurement of both short and long term. Hence the isotope unit "δ" (equation 1) was created that expresses the relative difference, in ‰, between the isotopic ratio of a sample and that of a standard.

$$\delta (\text{‰}) = \frac{{}^{18}\text{O}/{}^{16}\text{O}_{\text{sample}} - {}^{18}\text{O}/{}^{16}\text{O}_{\text{reference}}}{{}^{18}\text{O}/{}^{16}\text{O}_{\text{reference}}} \quad (1)$$

In the case of water, the reference is a sample of ocean water named SMOW (Standard Mean Ocean Water) delivered by the Agence Internationale de L'Energie Atomique (A.I.E.A., Vienne, Austria). Concentrations of oxygen 18 and deuterium in "SMOW" are 2005.2 and 155.8 ppm, respectively. The scale "δ" allows, in particular, to compare each other samples with very close isotopic concentrations.

In general, the water vapor is depleted in heavy isotope with respect to the liquid phase. There is also a wide variation in isotope content in the liquid phase, related to the nature of the compartment and its biogeochemical history. The residual water of liquids subjected to evaporation is more concentrated ("enriched") in heavy isotopes than the liquid itself.

Heavy water isotopes are affected by thermodynamic (equilibrium) or kinetic (no equilibrium) processes which are largely responsible for changes in concentration of these isotopes.

In an isotope exchange reaction between two substances A and B that contain the same element, or between the same substance A (water) present in two phases (liquid L, vapor V), it is possible to characterize the isotope discrimination. The isotope discrimination established during this reaction, is characterized by the isotopic fractionation factor "α". The factor α can be expressed as the quotient of ratios of A and B, or both phases of the substance A:

$$\alpha_{A/B} = \frac{R_A}{R_B} \text{ ou } \alpha_{L/V} = \frac{R_L}{R_V} \quad (2)$$

For the sake of convenience, we use the isotopic enrichment factor "ε" of A relative to B:

$$\varepsilon_{A/B} = (\alpha_{A/B} - 1) 10^3 \text{ ou } \varepsilon_{L/V} = (\alpha_{L/V} - 1) 10^3 \quad (3)$$

## 2.2. Isotopic fractionation related to evaporation

Several aspects of the isotopic fractionation of water in the soil-plant-atmosphere system have already been discussed in the literature.

Guntz and Beltran (1939) underlined that "Some living biological systems appear to produce partial water fractionation. The water from wood, leaves and sap, is heavier than ordinary water. This density increase could be attributed to difference of evaporation of heavy water compared to the light one, and may be, to the different distribution of heavy and light water across cell complex".

This isotopic fractionation was also highlighted for oxygen 18 of leaf water (Gonfiantini *et al.*, 1965). In a study of the isotopic composition of water in oak trees, Förstel *et al.* (1975) showed that the content of oxygen18 in water of branches remains identical to that of the soil water. In woody species, the transfer of water between soil and leaves therefore does not cause isotopic fractionation. During a

daily cycle, the same authors showed that the maximum observed in the isotopic composition of water of the leaves coincided with the optimum climatic conditions for transpiration.

Following this work, we can consider that the transfer of water in plants is accompanied by an identifiable isotopic fractionation of water in the leaf reservoir. Fractionation is attributed to the evaporation of water. Also, it is not surprising that the isotopic model applied to the leaf transpiration water reservoir takes into account factors already identified as part of the isotopic study of open water reservoirs in the process of evaporation.

The approach adopted by Craig and Gordon (1965) is the first from which were derived all models proposed later in the literature. This model takes into account the mass and isotopic balances involved in the exchanges across the liquid-vapor interface. The evaporation system is broken down into successive regions with a specific transfer process. Conventionally, five regions can be distinguished. Beyond these areas, the "free" atmosphere is no longer influenced by the evaporation process. Its relative humidity and its stable isotope content are freed from those of the vapor supplied by the local water reservoir.

In the atmosphere, these authors defined each region as:

- A relative humidity, normalized to the temperature and to the pressure of the vapor-liquid interface and a specific isotopic composition.
- A resistance to diffusion imposed by the specific transfer mode.

Therefore, during the evaporation process, a water molecule will pass successively through five layers from bottom to top:

(1) A zone " $L_T$ " where liquid mass transfer is effected by turbulent diffusion and whose isotopic composition remains uniform.

(2) A liquid film " $L_M$ ", where the mass transfer is assumed to operate solely by molecular diffusion.

(3) An interface " $I$ " in which moisture is considered saturated. The interface is the field of water and isotopic vapor-liquid equilibrium. The direct diffusion flux equals the backscattering in terms of flux of mass balances. Due to the differences between the saturated vapor pressures of the different isotopic species of water, the liquid will lose preferentially the lighter isotope in the gaseous phase and, therefore, the residual liquid phase will be enriched in the heavy isotopes. This discrimination will be characterized by an isotopic fractionation factor at equilibrium between water and vapor.

In the temperature and pressure ranges considered in this work, the isotopic fractionation factor at equilibrium was thermo-dependent. This is a monotonic function that decreases as a function of the temperature of the interface.

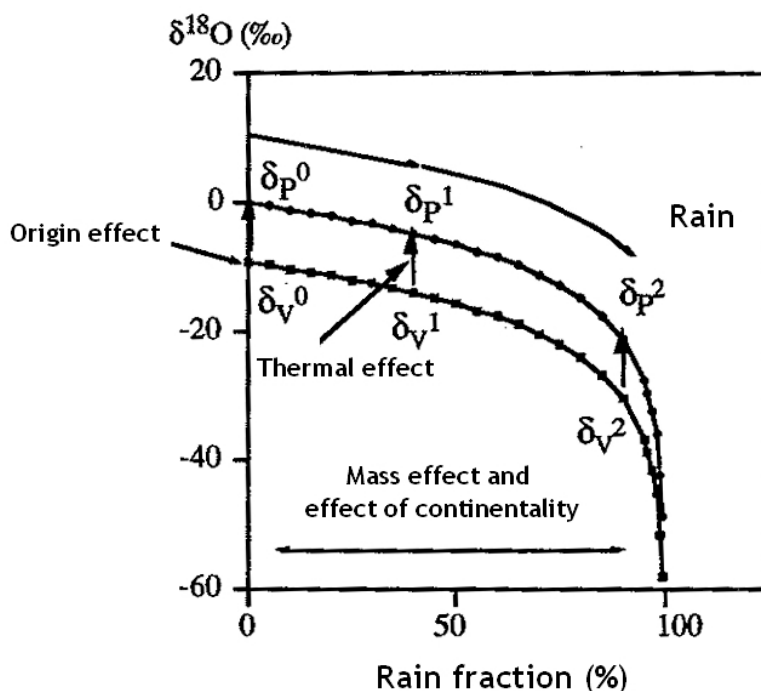
(4) A vapor film " $V_M$ ", field of molecular diffusion, where transfers are made in accordance with Fick's first law. In this layer, there is an additional effect attributable to the isotopic differences that exist in the molecular diffusion coefficients of the isotopic species of water vapor in the air.

(5) A vapor layer " $V_T$ ", domain of turbulent diffusion. The crossing of this layer does not cause isotopic fractionation: in fact, resistances to turbulent diffusion are equal for the different isotopic species. In addition to this evaporation flow oriented towards the atmosphere is associated a reverse diffusion flow, directed from the vapor to the liquid ("backscatter flow"). This flow causes the condensation at the surface of the liquid of water molecules coming from the gaseous phase. This addition of water

vapor molecules depleted in heavy isotopes, is responsible for limiting the isotopic enrichment of water in all evaporative phenomena.

### 2.3. Isotopic fractionation related to condensation

During rain events, the formed liquid fraction is enriched in the heavy isotopes relative to the residual gas fraction within the cloud. The changes in isotopic composition of the gas phase and the resulting liquid phase can be interpreted very schematically through the Rayleigh distillation (Figure 1, Dansgaard, 1964).



**Figure 1.** Comparative evolution of  $^{18}\text{O}$  contents of residual water vapor inside a cloud and in rain coming from this cloud as a function of precipitated rain.

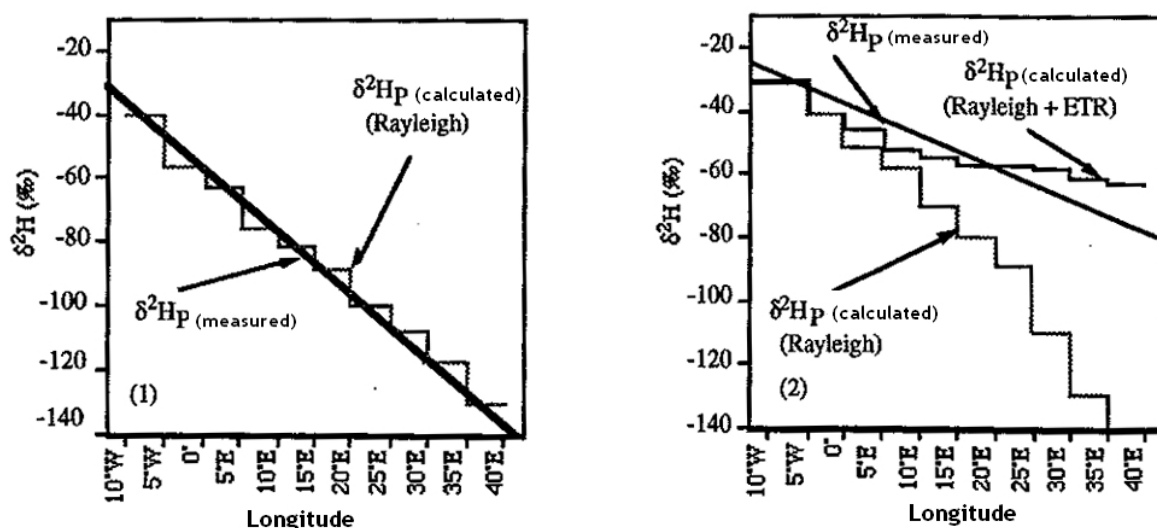
At a given time, the isotopic composition of the initial liquid fraction ( $\delta_L^0$ ) leaving the cloud base, is in equilibrium with that of the original vapor ( $\delta_V^0$ ), that gave birth to this liquid. The raindrops (enriched in the heavy isotopes) leaving the cloud impose an isotopic depletion to the residual water vapor in the case where the cloud is not replenished by the surrounding atmospheric vapor ("Reservoir effect").

At each new episode of condensation corresponds a precipitation whose isotopic composition ( $\delta_L^1$ ) is in equilibrium with isotopic composition of the vapor ( $\delta_V^1$ ). Therefore, this new precipitation has a heavy isotope content lower than that of the first precipitation ( $\delta_L^1 < \delta_L^0$ ). This process is repeated each time a new precipitation occurs. In the case mentioned above, it was assumed that the condensation temperature was the same in the cloud, which results in a constant gap between the isotopic abundance of the residual vapor and the precipitated liquid fraction.

Draining the atmospheric vapor reservoir therefore results in a gradual decrease in the isotopic composition of atmospheric vapor originated from ocean and of rain derived from different condensation episodes. Different isotope effects may be highlighted:

- "Origin effect": The isotopic composition of the initial water vapor is dictated by the origin of the air mass. Air masses formed over the Atlantic Ocean does not have the same isotopic composition as the air masses formed over the polar ocean areas.
- "Thermal effect": The condensation process in the clouds uses, among others, the differences of saturated vapor pressure, and thus the temperature. The gap between the isotopic composition of the vapor and the isotopic composition of rain, will therefore also be controlled by the precipitated amount of rain.
- "Mass effect": The evolution of the isotopic composition of two phases is controlled by the precipitated amount of rain.

This mass effect will generate a continentality effect that has, in particular, been highlighted in isotopic gradients of precipitations in Western Europe (Figure 2). Rozanski *et al.* (1982) showed that in winter it was possible to simulate, through a drain effect of heavy isotopes in vapor of clouds (as mentioned above), the isotopic evolution of rainfall recorded on ground between Ireland and Austria (Figure 4). However, when applying the same type of model to summer rainfall, there is a significant bias between the contents calculated from the vapor drain model, and the contents of deuterium or oxygen 18 measured in precipitations (Figure 2). Indeed, one of the assumptions of atmospheric discharge model is not true: there is a recycling of local vapor of continental origin in vapor of oceanic origin. This local vapor, which is produced by evapotranspiration, must have a higher isotopic composition than that of the oceanic value.



**Figure 2.** Evolution of continentality effect (measured and calculated from a type of Rayleigh distillation model) in the European winter (1) and summer (2) precipitations (Rozanski *et al.*, 1982).

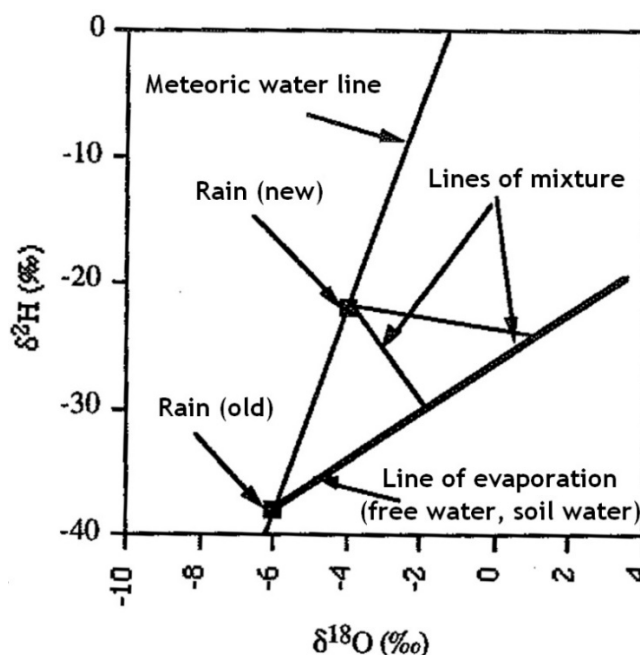
#### 2.4. $^2\text{H} - ^{18}\text{O}$ diagram

A specific linear relationship combines oxygen levels to those of deuterium measured in precipitation (Craig, 1961). The straight line called "meteoric water line" thus obtained has a slope of 8 and a y-intercept of 10 ‰ in a diagram  $\delta^2\text{H} - \delta^{18}\text{O}$  (Figure 3). The value of the parameters of this line is imposed

by climate parameters that govern evaporation from the oceans and is characteristic of the process of condensation.

This allows to directly identify the origin of water samples taken, for example, in deep aquifers whose isotopic compositions are arranged along this type of water line. Isotopic analysis allows to show that these samples kept same signature as that of the rain. These samples, which have thus escaped a takeover by evaporation, have a signature which allow us to conclude to a quickly seep of rain towards deeper saturated areas.

Indeed, in the case of evaporation (Craig, 1961), *op. cit.*, the evolution of the isotopic composition of water of a reservoir is represented in a diagram  $\delta^2\text{H} - \delta^{18}\text{O}$  by a line named "evaporation line" characterized by a slope with a value (2 to 4) less than that of the meteoric water line (Figure 3).



**Figure 3.** Meteoric water line, evaporation line and mixtures in a  $\delta^2\text{H} - \delta^{18}\text{O}$  diagram.

Another family of lines named "mixture line", characteristic of a mixing process between the water related to precipitation and water under the control of evaporation, can also be observed in this diagram  $\delta^2\text{H} - \delta^{18}\text{O}$  (Figure 3).

### 3. THE ASSUMPTION OF THE ISOTOPIC PATTERN OF TRANSPIRATION

A literature review shows that 5 assumptions are the basis of the transpiration model:

- (1) No isotopic fractionation of soil water in the root absorption (Zimmermann *et al.*, 1967), which implies an identity between the isotopic composition of water from the soil and the water from the roots.
- (2) Equality of flow of transpiration and of root absorption within the plant (Förstel, 1978).
- (3) Homogeneity of the isotopic composition within the leaf reservoir (Dongmann *et al.*, 1974).
- (4) Permanence of stationary water isotopic states within the leaf reservoir (Allison *et al.*, 1985).

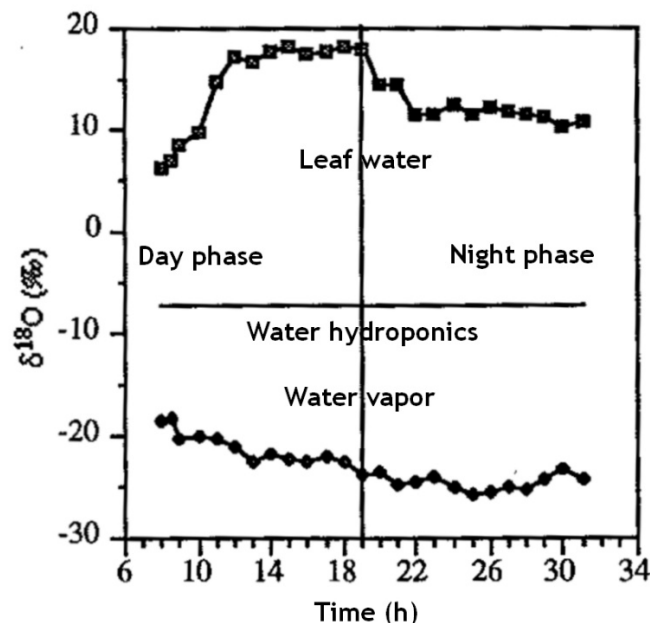


(5) Homogeneity of the isotopic composition of atmospheric water vapor that participates in exchanges with the leaf water reservoir (Dongmann *et al.*, 1974, *op. cit.*).

Various studies on these assumptions have shown that:

- Assumption (1) was checked regardless of soil moisture. We therefore consider that root uptake does not cause isotope discrimination of soil water.
- Assumption (2) has been called into question because of the existence of internal reserves in the plant. But we can assume that this water, in direct contact with sub-stomatal cavities, is in permanent water regime: losses due to evaporation of water are directly offset by root pumping (Walker *et al.*, 1989) or by internal water reserves the plant.

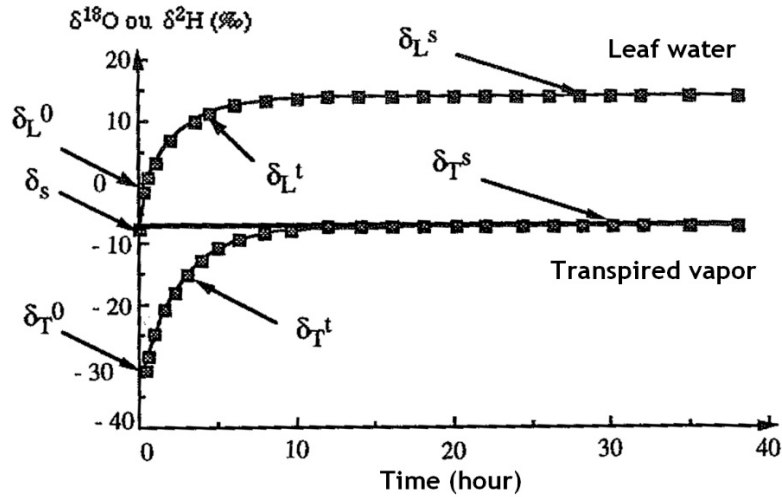
In this case, when the environmental conditions are kept constant, we can simulate the temporal evolution of the isotopic composition of liquid and gaseous phases of the leaf reservoir (Figure 4) where  $\delta_L^0$  is the isotopic content of water reservoir before evaporation.  $\delta_L^t$  characterizes the succession of  $^{18}\text{O}$  contents over time that are increasingly enriched in the heavy isotope due to transpiration.  $\delta_L^s$  defines the isotopic composition of water from the reservoir that overcomes the time variable "dynamic equilibrium".



**Figure 4.** Changes with time of the  $^{18}\text{O}$  content in leaves, in water hydroponics and in water vapor during a circadian cycle.

So we met successively an initial isotopic state, different transient state, and then a steady state. Note that obtaining an isotopic steady state necessarily requires the existence of a permanent water regime in the reservoir which undergoes evaporation, while reciprocity is inaccurate, because a permanent water regime does not necessarily correspond to an isotopic stationary state (Figure 5).

$\delta_L^0$ ,  $\delta_L^t$ ,  $\delta_L^s$  are the isotopic compositions of water of the foliar reservoir calculated in the initial, transient and stationary state, respectively.



**Figure 5.** Theoretical evolution of the oxygen-18 content of the leaf water reservoir and of the water vapor coming from this reservoir (Bariac *et al.*, 1990; Bariac *et al.*, 1991).

$\delta_L^0$ ,  $\delta_L^t$ ,  $\delta_L^s$  are the isotopic composition of transpired water by leaf calculated in the initial, transient and stationary state, respectively.

$\delta^{18}O_s$  is the isotopic composition of water supplying the foliar water reservoir.

Over time, changes in the isotopic composition of leaf water is described by equation (4) where  $\delta_L^t$  is expressed in part to 1:

$$\delta_L^t = \delta_L^s - (\delta_L^s - \delta_L^0) e^{-\left(\frac{\tau}{\varepsilon}\right)(t-t_0)} \quad (4)$$

with:

$\tau$  = turnover of foliar water reservoir (equation 5):

$$\tau = \frac{\phi\tau}{(1-V_0)} \quad (5)$$

$\phi$  = transpiration flux;

$V_0$  = leaf water reservoir really submitted to transpiration;

$\delta_L^0$  = initial isotopic composition of leaf water at time  $t_0$ ;

$\delta_L^s$  = isotopic composition of leaf water calculated at steady state using the relation (6):

$$\delta_L^s = \varepsilon(\delta_s + 1) + h(\delta_v + 1)(\varepsilon_e + 1) - 1 \quad (6)$$

where:

$$\varepsilon = (\varepsilon_e + 1)(\varepsilon_k + 1)(1 - h) \quad (7)$$

and:

$\delta_s$  = isotopic composition of water supplying leaf.

$\delta_v$  = Isotopic composition of the atmospheric water vapor, submitted to an exchange with the leaf water reservoir.

h = Atmospheric relative humidity standardized to temperature and pressure of liquid-vapor interface.

$\epsilon_e$  = Isotopic enrichment factor at equilibrium, related to differences between the saturated vapor pressures of the various isotopic species of water vapor in the air.

$\epsilon_k$  = Kinetic isotopic enrichment factor related to differences between the diffusion coefficients of the isotopic species of water vapor in the air.

The formulation presented in equations (4) and (7) is widely used in the literature since the establishment of model of Craig and Gordon.

The isotopic composition of the vapor from transpiration of sub-stomatal cavities has a similar development (Figure 5). The isotopic composition of the vapor is given by the following relationship:

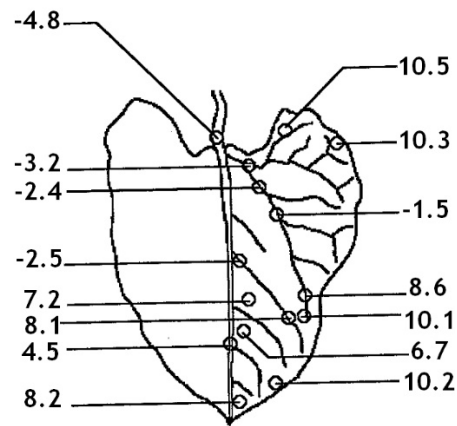
$$\delta_E^t = \frac{(\delta_L^t + 1) - h(\delta_v + 1)(\epsilon_e + 1) - \epsilon}{\epsilon} \quad (8)$$

A particularly interesting property which will be discussed below, is that at steady state, isotopic composition of the vapor coming from the evaporation system (and not that of the ambient water vapor) tends to a content which is the content of water supplying the reservoir and subject to evaporation (equation 9):

$$\delta_E^t = \delta_S \quad (9)$$

Despite a change of liquid-vapor phase, and regardless of the value of  $\delta_L^S$  imposed by environmental conditions, the isotopic composition of the transpired water vapor is therefore identical to that of the water entering the leaf. Therefore at isotopic steady state, the plant behaves as a simple wick in the transfer of water in the atmosphere.

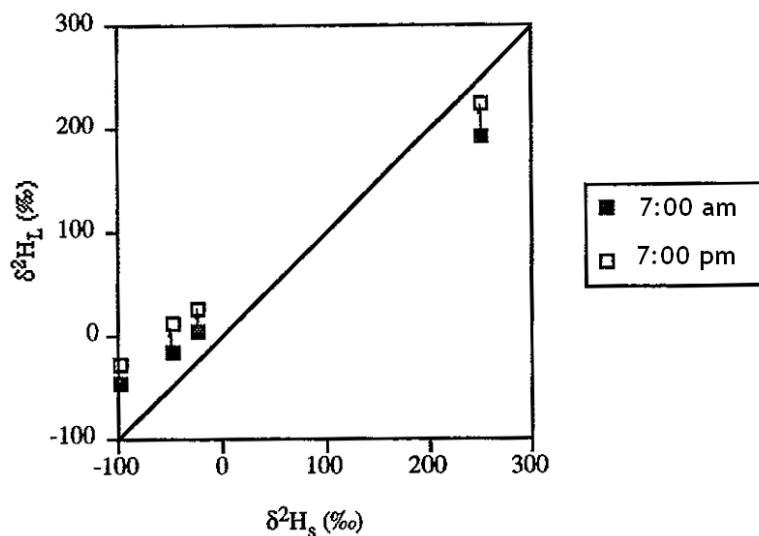
- Assumption (3) was proved to be inaccurate (Bariac *et al.*, 1994a): for example, performing an  $^{18}\text{O}$  content mapping within a primary leaf of bean demonstrated the existence of two isotopic gradients (Figure 6) between the basal and apical portions of the leaf, and between the median rib and the edge of the leaf. This can be interpreted as a simple problem of mixture of waters with different geochemical stories;
  - (a) Xylem sap is representative of the isotopic history of water in the soil and therefore of rainfall more or less taken by evaporation.
  - (b) Phloem sap is enriched in heavy isotopes due to transpiration.
- Assumption (4) is not always verified at the scale of a circadian cycle, due to the fact that water of the leaf reservoir is not instantaneously at isotopic steady state (Figure 5), in particular, during the first hours of the day, then at the end of the day and during the night, i.e. when the flux of transpiration shows the lowest values (low level of turn-over of the leaf water reservoir).
- Assumption (5) is not verified either, due to the fact it exists a strong spatial and temporal variability of the heavy isotope content in vapor (Bariac, 1988). This requires a continuous measurement of the isotopic composition of water vapor in experiments conducted in the soil-plant-atmosphere continuum.



**Figure 6.** Mapping the water oxygen content in a primary leaf taken from a bean plant (Bariac *et al.*, 1994a). The  $^{18}\text{O}$  content of irrigation water was  $-7.2\%$ .

#### 4. ISOTOPIC SIGNATURE OF THE WATER FILLING THE LEAF: CONSEQUENCE FOR DETERMINING THE AVERAGE ZONE OF ROOT UPTAKE

A first experiment is to progressively enrich with deuterium or oxygen-18 water of hydroponic cultures placed in the same environment, and to simultaneously track the isotopic composition of water from leaf samples taken at 7:00 am after 12 hours of exposure to the dark, and at 7:00 pm after 12 hours of exposure to light (Bariac *et al.*, 1994a, op. cit., figure 7).



**Figure 7.** Change of the isotopic composition of the leaf water of bean plants as a function of the isotopic composition of the irrigation water. Leaf samples have been taken after 12 hours of photoperiod ("7:00 pm") or after night ("7:00 am").

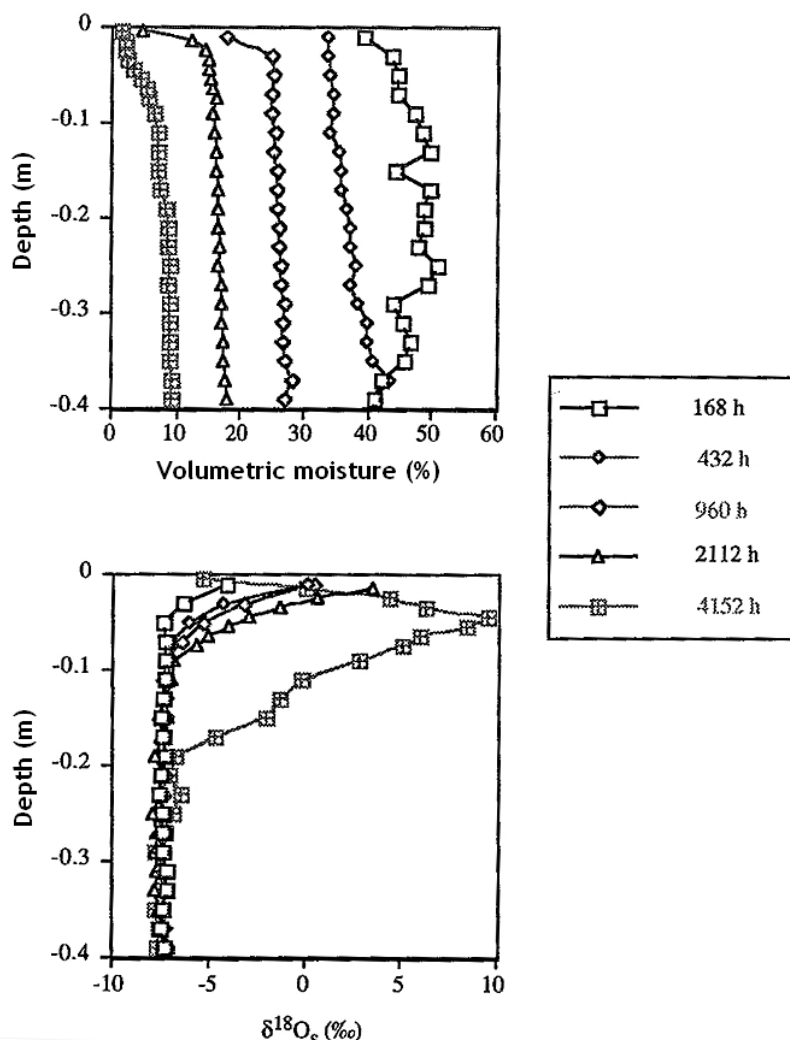
Three types of results are shown in Figure 7.

- The night foliar water is more concentrated in heavy isotopes than the morning one due to transpiration.

- The increase in heavy isotopes concentration of the hydroponic solution causes the increase of leaf water one either evening or morning. There is a linear relationship between the day or night isotopic compositions and those of the irrigation water.
- The obtained linear regression curves thus do not coincide with the bisector of the figure 7. This means that the isotopic composition of soil water has an influence on that of the leaf reservoir, but one or other processes are also involved. In particular, for very high levels of heavy isotopes of hydroponics, the isotopic composition of leaf water becomes lower than that of the irrigation water, either in the evening or morning. The process thus implicated in this phenomenon is the return (back scattering) of vapor to liquid and thus the resulting limitation of the enrichment of the isotopic composition within the leaf water reservoir.

#### 4.1. Isotopic composition of soil water and water of roots

A new experiment was carried out in the laboratory on homogeneous soil columns, drained for several days, to obtain a density and a stable isotope moisture content roughly constant over the entire length of the column (Boujamloui, 1994, figure 8).



**Figure 8.** Change with time of the isotopic profile ( $\delta^{18}O$ ) of water inside soil columns submitted to evaporation and without water supply. Note: Profiles were previously homogenized for water and heavy isotopes contents (Boujamloui, 1993).

Then these columns were dried out to the air without refueling. Gradually, the volumetric moisture of these columns decreased: This effect was more sensitive to the soil surface where evaporation occurs. Simultaneously, measurement of levels of heavy water isotopes highlighted the existence of isotopic gradients more pronounced with time.

In depth, capillary rise did not lead to an isotopic discrimination and isotopic signal remained homogeneous and identical to that of water used to fuel the columns.

After a certain time (4152 hours in our experiment) the amount of water present in the liquid phase in the pores of the soil was sufficiently reduced in the surface layers. The influence of the gas phase of the soil and of the outside atmospheric vapor became then noticeable: inverse isotopic gradients could be observed in water and surface soil layers due to isotope exchange between the liquid phase and the gas phase whose isotopic contents are different.

Soil can therefore have a high spatiotemporal heterogeneity as to its content of heavy isotopes (Barnes and Allison, 1983). At this heterogeneity is superimposed that of the root system may take water at different depths. A soil sample can in no way be representative of the supply signal of the plant under natural conditions.

#### **4.2. The method of evaporation lines**

Craig (1961, op. cit.) proposed a method that allows the determination of the heavy isotope content of water that fills a reservoir without the need to measure directly this content. It is the method of evaporation lines in a  $\delta^2\text{H} - \delta^{18}\text{O}$  diagram. For example, there is the case of water reservoirs whose isotopic composition is the same and belongs to the meteoric water line (= rain out evaporation). These reservoirs are submitted to evaporation and the isotopic composition of water of these reservoirs are determined progressively as the amount of water decreases. An evaporation line (slope ranging between 2 and 4) can be described in a  $\delta^2\text{H} - \delta^{18}\text{O}$  diagram.

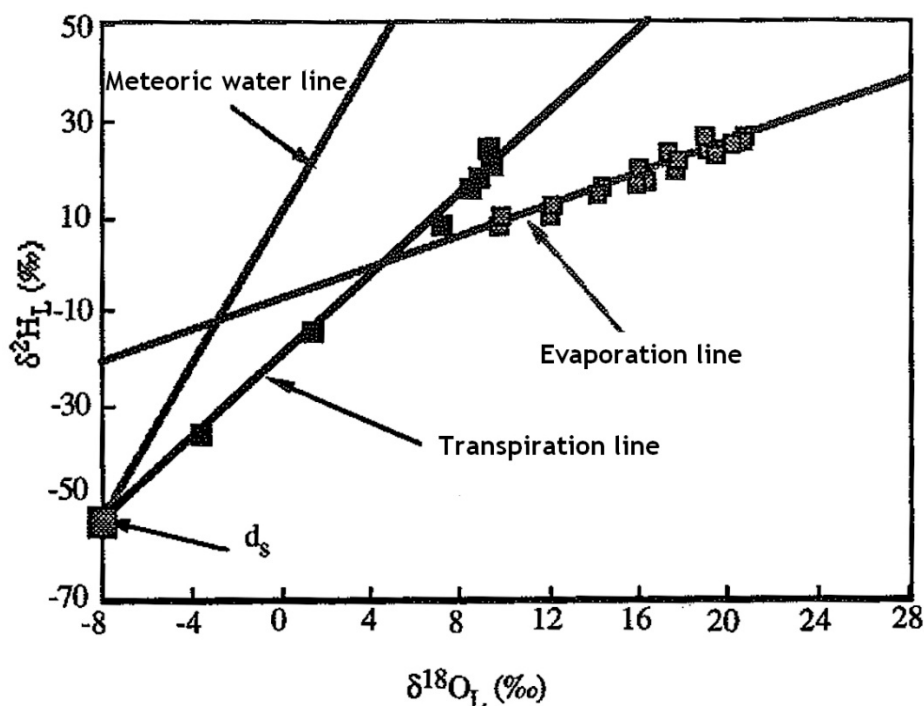
An important property of stable isotopes of water is that the intersection between the evaporation line, experimentally established, and the meteoric water line gives access to the heavy isotope content of water supplying a reservoir before its evaporation. This was observed only in the case where this water has kept same isotopic signature as rain before filling the reservoirs. This is interesting because it is generally difficult to have access to the entire history of water in the reservoir (like a lake, for example). We will then consider only part of the evaporation story of the reservoir, which will give access to a segment of the evaporation line in a  $\delta^2\text{H} - \delta^{18}\text{O}$  diagram. We will just need to virtually extend the line segment in this type of diagram: its intersection with the meteoric water line will provide the isotopic composition of the water of this reservoir before evaporation.

This method is commonly applied in isotope hydrology and hydrogeology, for example in the case of determining the content of heavy isotopes of rains recharging groundwater.

#### **4.3. The method of transpiration lines**

In contrast, the method of evaporation lines cannot be applied to the process of transpiration (Allison *et al.*, 1985).

To explain this apparent contradiction between these two experiments, we must consider the control exercised by the relative humidity (normalized to the interface temperature) on isotopic states of a water reservoir in permanent water regime situation (Figure 10).

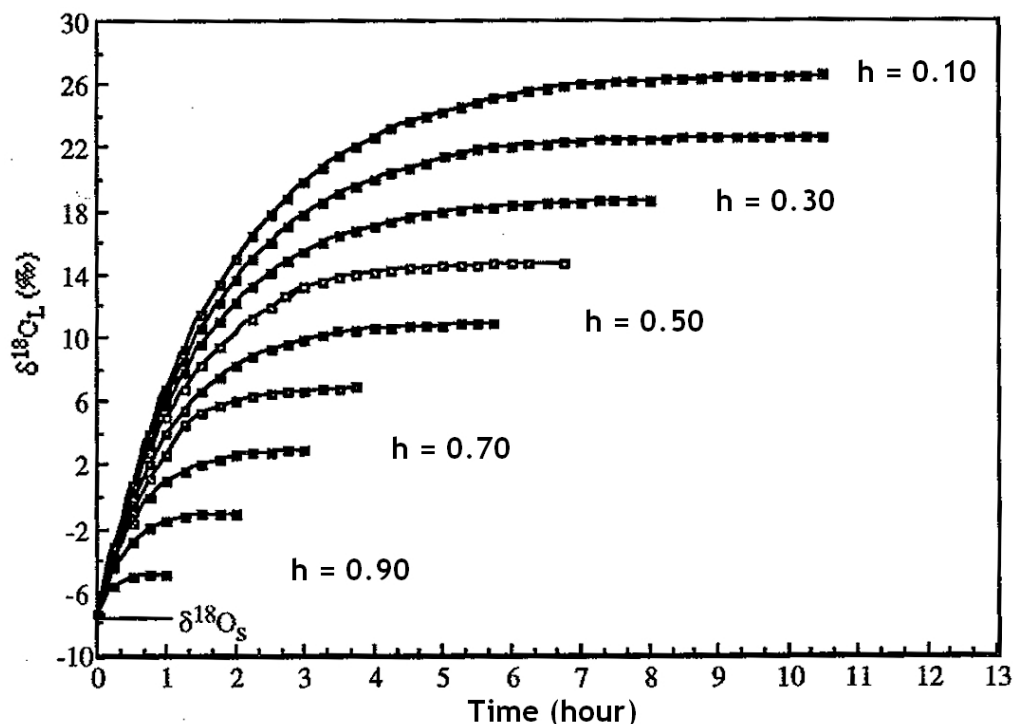


**Figure 9.** Presentation in a  $\delta^2\text{H}$ -  $\delta^{18}\text{O}$  diagram of the evolution of the isotopic composition of water samples of different nature (open water reservoirs and leaves of terrestrial plants) placed in the same climatic environment (Bariac, 1988). The filling water of the two types of reservoirs has the same isotopic composition. The meteoric water line " $\delta^2\text{H} = 8 \delta^{18}\text{O} + 10$ " is also represented.

Figure 9 shows, in the  $\delta^2\text{H}$ -  $\delta^{18}\text{O}$  diagram, two simultaneous experiments of evaporation of open water reservoir and of bean leaf transpiration placed together in the same environmental conditions (controlled environment). The water (measured) has the same isotopic composition in the two experiments. Evaporation (open water) or transpiration (bean) lines obtained are then extended to the intersection with the meteoric water line. The results show that we can determine the isotopic composition of the filling water ( $\delta_s$ ) from open water reservoirs before evaporation while this is not possible in the case of transpiration line. This is valid after comparison between the calculated and measured values.

In general it is seen that the greater the relative humidity decreases, the greater the content of heavy isotopes increases (Figure 10). If we want to simultaneously describe this evolution for the two heavy isotopes of water in a  $\delta^2\text{H}$ -  $\delta^{18}\text{O}$  diagram, we will represent successively for the same relative humidity (Figure 11):

- The initial isotopic state (filling water whose isotopic composition belongs to the meteoric water line) which is identical for the different isotopic changes controlled by the different values of relative humidity.
- The different values of the isotopic transient states.
- A stationary isotopic state characterized by a single point in a diagram, in so far as in the steady state, the isotopic composition of water overcomes the temporal variations.



**Figure 10.** Time evolution of the isotopic composition of water of the foliar reservoir for different relative humidity values ( $h$ ) normalized to the temperature of the leaf surface.

Different values of relative humidity lead to the production of families of lines in a  $\delta^2\text{H}$ -  $\delta^{18}\text{O}$  diagram. Two families of lines can thus be distinguished:

- Segments of lines that characterize the isotopic transient states whose slope is governed by the relative humidity. These segments are defined on the one hand, by the isotopic composition of the initial state of the water before the evaporation reservoir (isotopic composition of the feed water) and on the other hand, by the isotopic composition calculated at the steady state.
- A segment of line that characterizes the isotopic stationary states. This segment is bounded, on the one hand, by the isotopic composition determined in the steady state of saturation vapor pressure (=liquid - vapor isotopic equilibrium) and, on the other hand, by the calculated isotopic composition at steady state in the extreme case where the relative humidity is 0. The virtual extension of this line segment and its intersection with the meteoric water line does not give access to the isotopic composition of the water reservoir before evaporation.

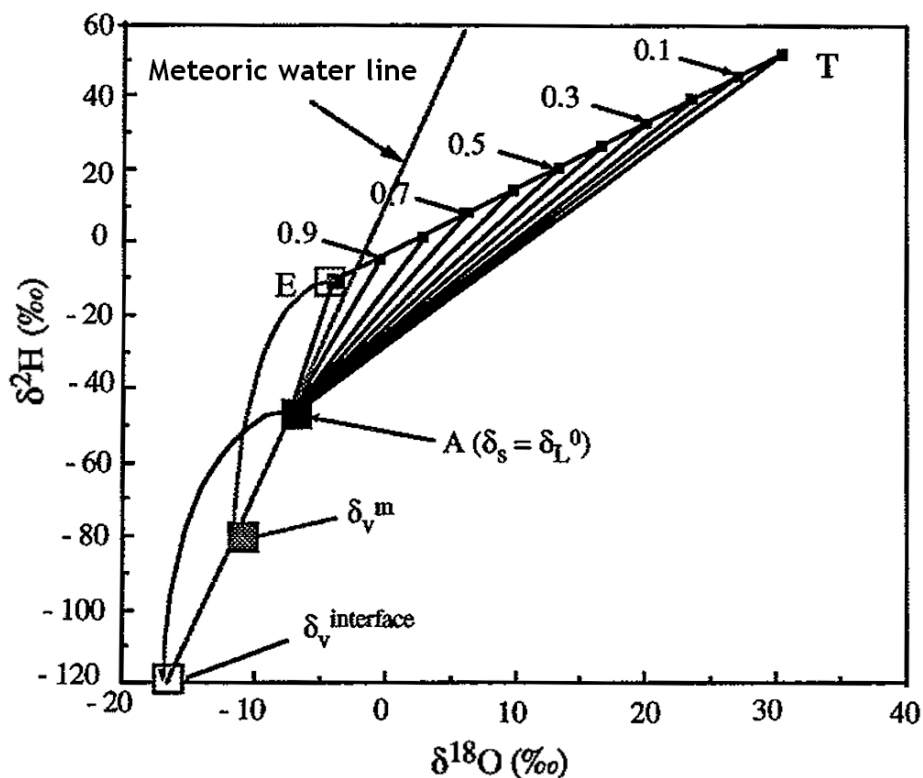
Two families of lines are distinguished (Bariac, 1988):

(1) The line of isotopic stationary states ( $\delta_L^s$ ) whose virtual extension, and its intersection with the right of meteoric waters, does not allow to determine the isotopic composition of the filling water ( $\delta_s$ ). Note that the normalized relative humidity ( $h$ ) to the temperature of the leaf area does not affect the slope of this line.

(2) The lines of isotopic transient states ( $\delta_L^t$ ). The virtual extension of one of these lines and its intersection with the meteoric waters allows to determine the isotopic composition of the water filling



( $\delta_s$ ) the leaf reservoir, if it is not subject to evaporation. Note that the normalized relative humidity to the temperature of the leaf surface strongly influences the slope of these lines.



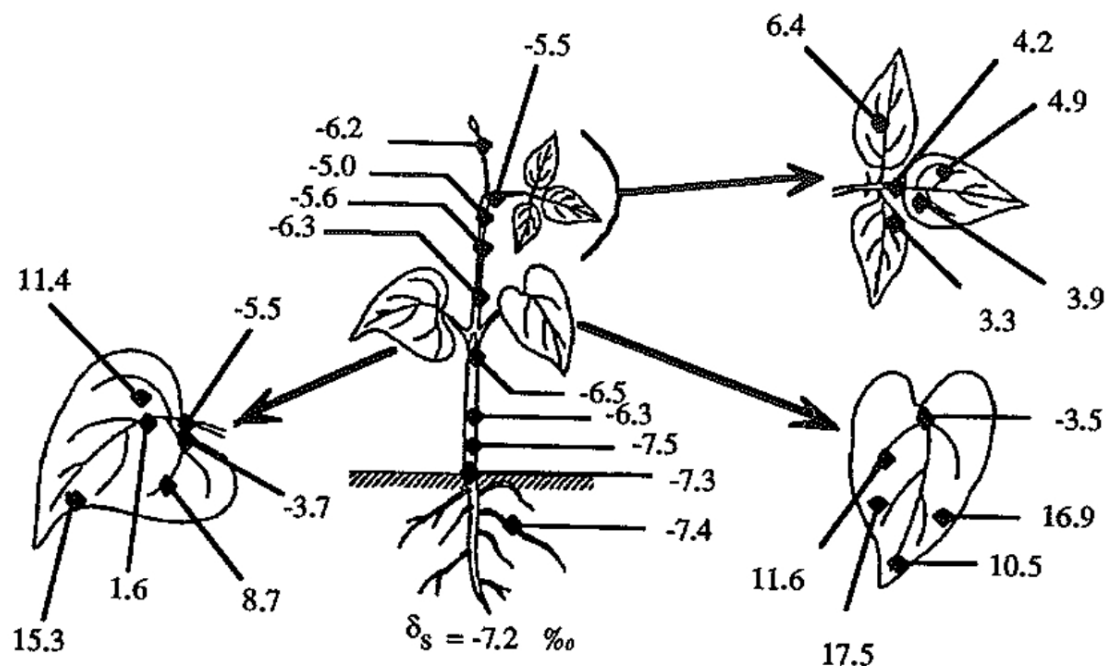
**Figure 11.** Meteoric water line and transpiration lines in a  $\delta^2\text{H}$ -  $\delta^{18}\text{O}$  diagram

The isotopic compositions of the measured vapor ( $d_v^m$ ) and one that is in equilibrium ( $d_v^{\text{equilibrium}}$ ) with the filling water are represented.

If we compare the amount of water flowing through the leaf to the amount of water present in the same leaf, we see that the renewal rate of the volume of leaf water is generally very high and will quickly impose an isotopic steady state. Due to the change in relative humidity, the isotopic composition of a foliar water reservoir will describe successively different isotopic stationary states. Therefore the content of heavy water isotopes in water supplying foliar reservoir cannot be determined. It will therefore impose to measure the isotopic composition of water filling the foliar reservoir.

#### 4.4. Isotopic composition of water in aboveground organs with little or no transpiration

A series of samples carried out in indoor hydroponics, thus preserved from evaporation, helps to demonstrate the existence of an isotopic gradient in the distribution of oxygen-18 in water of organs of a bean plant (Bariac *et al.*, 1994, *op. cit.*, figure 12). Oxygen levels increase gradually between roots and leaves where these levels reach their maximum values. The root has a water isotopic composition identical to that of the supplied water, which means that there is no isotopic fractionation during the passage of water from hydroponic cultivation to the roots. The other aerial parts (stem, petiole, rib) have intermediate levels close to that of the supplied water.



**Figure 12.** Evolution of the water oxygen content in the different organs of a bean plant. The isotopic composition of water of hydroponics is  $-7.2 \text{ ‰}$  (Bariac *et al.*, 1994a).

Increasing the oxygen-18 content in the water of aboveground organs subjected to little or no transpiration can be justified by the existence of two fluxes.

- The xylem sap which the isotopic labeling is imposed by the soil.
- The phloem sap which the isotopic labeling is imposed by that of the leaf transpiration.

The isotopic composition of the water circulating in the plant is the product of a double labeling. The samples include two types of sap and thus produce intermediate oxygen-18 levels observed in roots and leaves. The isotopic composition of water of these organs cannot be considered for the determination of the isotopic abundance of water supplying the foliar reservoir due to the artifact related to the sampling mentioned above. Using a simple mixing equation (equation 10) allows to determine the respective amounts of water coming from root uptake and transpiration at any point of the plant. Outside the ribs, the sap represents only a small percentage of water of aboveground organs not subjected to transpiration (less than 10%).

$$\delta_L^m = x\delta_L^T + (1 - x)\delta_S \quad (10)$$

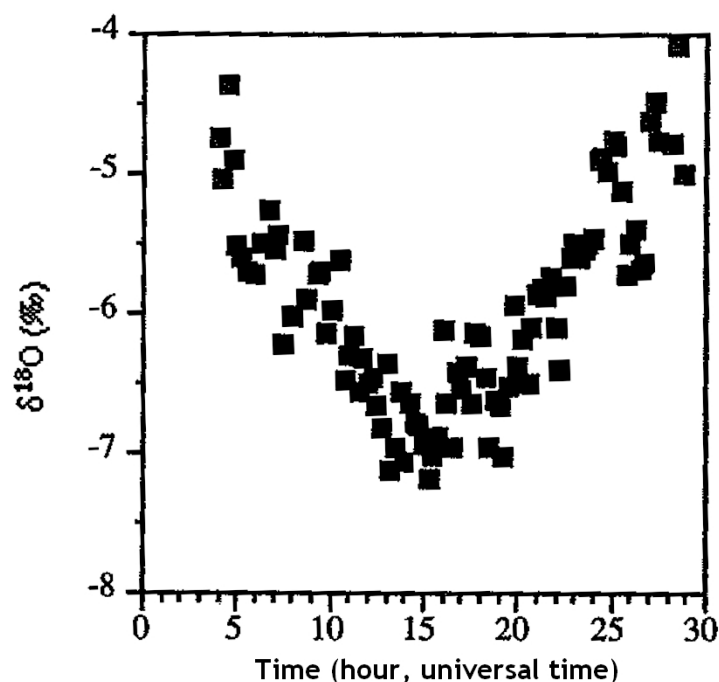
#### 4.5. Isotopic composition of water of the collar in a plant

These results lead to retain the isotopic composition of water of the collar (interface stem - root) as representative of the signal of the water entering the leaf. On the one hand, all the water taken up by the roots passes through this organ. So, this will enable us to incorporate the isotopic signal of the water taken from the ground. On the other hand, this organ may be relatively distant from the leaves and is therefore prone to a low or null contamination from the phloem sap.

A new experiment was conducted on maize plants grown with covered pot. Prior to sampling, the soil of this culture was carefully drained and irrigated with the same water to impose a uniform isotopic signal. The collar of these plants were collected for 14 hours to examine the isotopic evolution of their

water over time and to evaluate the influence of the phloem sap coming from leaves. Results show that the oxygen-18 content of collar water of maize plants was very stable over time. Through this experiment, we demonstrated there was no influence of the phloem sap on the isotopic signal of the collar water.

In experiments conducted in natural conditions, the oxygen-18 content of the water of the collar of wheat plants showed a clear evolution over time (Figure 13). The isotopic composition decreased during the day and then tended to return to its initial state during the night. The isotopic compositions of soil water measured at the same level did not show significant changes during the same period.



**Figure 13.** Evolution of the oxygen-18 content of collar water in wheat plants, sampled during a circadian cycle (Marrakech, Agronomy Unit of Haouz, 27 July 1989).

Isotopic evolution of water from the collar could be performed by changing the amount of water pumped to different depths in the soil during the circadian cycle to the extent that the superficial soil layers have lower water contents and therefore are more enriched in the heavy isotope due to evaporation. Indeed, mobilization of water from the soil by the plant takes place where energy cost is the lowest. It can be assumed that a high transpiration stream matches the absorption of a greater amount of water in depth. During the night, the transpiration is minimal compared with daytime transpiration: the roots no longer have to mobilize significant amounts of water in depth; this would therefore result in a decrease in root absorption in depth and therefore at the collar, with a signature of water close to that of the topsoil.

Access to the isotopic composition of water of the collar thus make possible the determination of an “average” area of root pumping and allow monitoring the change in the amount of water pumped by the roots throughout a circadian cycle. This determination is only possible if there is:

- a root network well developed across the analyzed soil profile,

- A severe desiccation of the soil surface.
- An isotopic soil gradient depending on the soil depth. This gradient can be related to the temporal variation of the isotopic signature of different rains entering inside the ground, and / or alteration of the isotopic composition of these rains due to the evaporation of water from the surface layers of the soil.

## 5. ISOTOPIC COMPOSITION OF THE WATER OF THE LEAF RESERVOIR

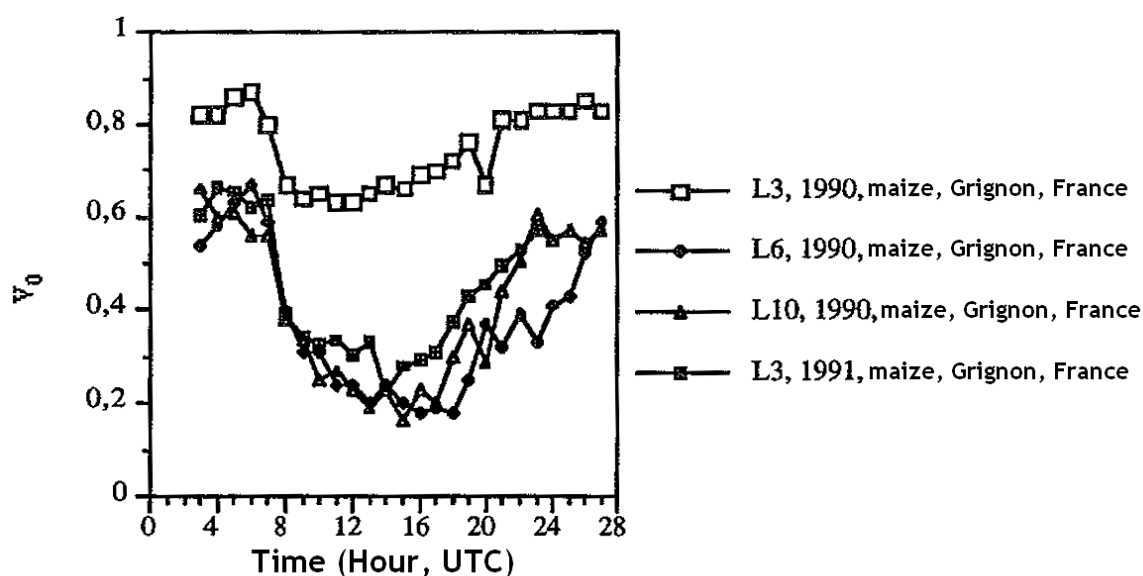
### 5.1. Time evolution of the amount of unlabeled water by transpiration

To take into account the spatial heterogeneity of the isotopic composition of the foliar water reservoir mentioned above, Leaney *et al.* (1985) proposed a mixture model (equation 5) that distinguishes two types of sub-reservoirs according to their geochemical history. To achieve this deal, these authors used information provided by the vacuum distillation of the water of leaves:

- The sub-reservoir ( $V_0$ ) unlabeled by transpiration and whose the isotopic composition is imposed by the soil water. This labeling is the result of history of precipitation, infiltration and evaporation; the isotopic composition of water of the collar is representative of this labeling.
- The sub-reservoir ( $1 - V_0$ ) labeled by transpiration.

$$\delta_L^m = V_0 \delta_{collar} + (1 - V_0) \delta_L^T \quad (11)$$

It thus becomes possible to calculate the proportion of leaf volume ( $V_0$ ) which is not labeled in heavy isotopes by transpiration. From the various measured parameters in natural conditions and from the isotopic model of transpiration, we can calculate the theoretical isotopic composition of water of the reservoir labeled by transpiration. Then, we compare these theoretical values with those measured in the leaf. The difference between the measured and calculated values is due to the underestimation of the isotopic composition of the leaf due to water extraction methods water of whole leaves, and so that there was a fraction extracted from water ( $V_0$ ) which is not labeled by transpiration. This therefore makes it possible to follow the evolution of this fraction ( $V_0$ ) over time (Figure 14).



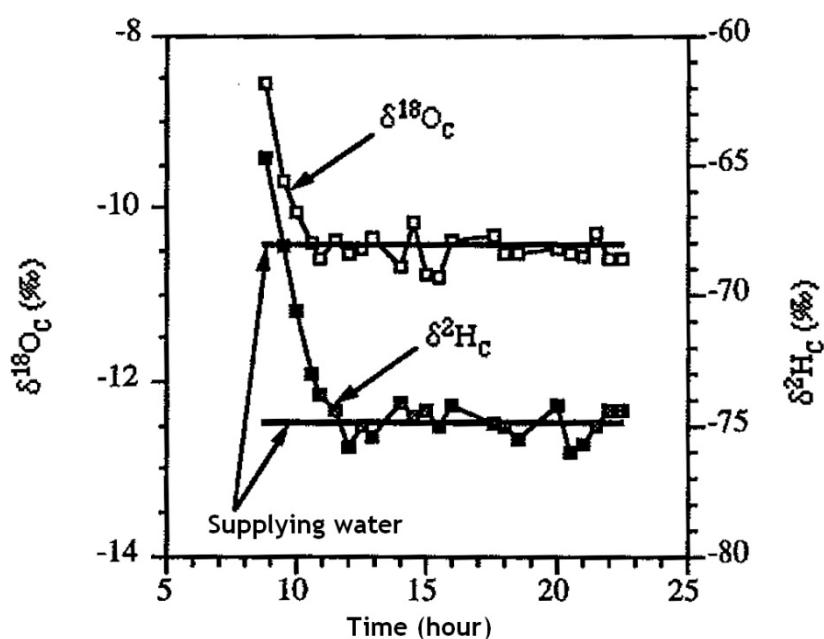
**Figure 14.** Evolution of the amount of water within the maize leaf reservoir unlabeled by transpiration relative to the transpiration request (Bariac *et al.*, 1994b).

During the day, the calculated value of the term ( $V_0$ ) varies over time and depends on weather conditions. This value decreases sharply when the evaporative demand is high. Conversely,  $V_0$  values are higher in the case of relatively low transpiring leaves. We thus find an inverse relationship between changes in  $V_0$  and the transpiration flow, which confirms the work of Walker *et al.* (1989) and Walker and Brunel (1990).

## 6. ISSUES ON THE ISOTOPIC SIGNATURE OF THE TRANSPIRED WATER VAPOR: CONSEQUENCES FOR THE ISOTOPIC WATER CYCLE

### 6.1. Highlighting the specificity of the isotopic signature of transpired water

Comparing the isotopic composition of the water of a leaf with the transpired water vapor (specific controlled chamber, C2 3A type) highlights the identity of isotopic water signatures of these two compartments. When the leaf water reaches a stationary isotopic status, simultaneously, the isotopic composition of the transpired vapor tends to a unique stationary status. This status is imposed only by the content of heavy isotopes of the water reservoir supplying the leaf (Figure 15), regardless of the stationary isotopic state reached by the water of the foliar reservoir.



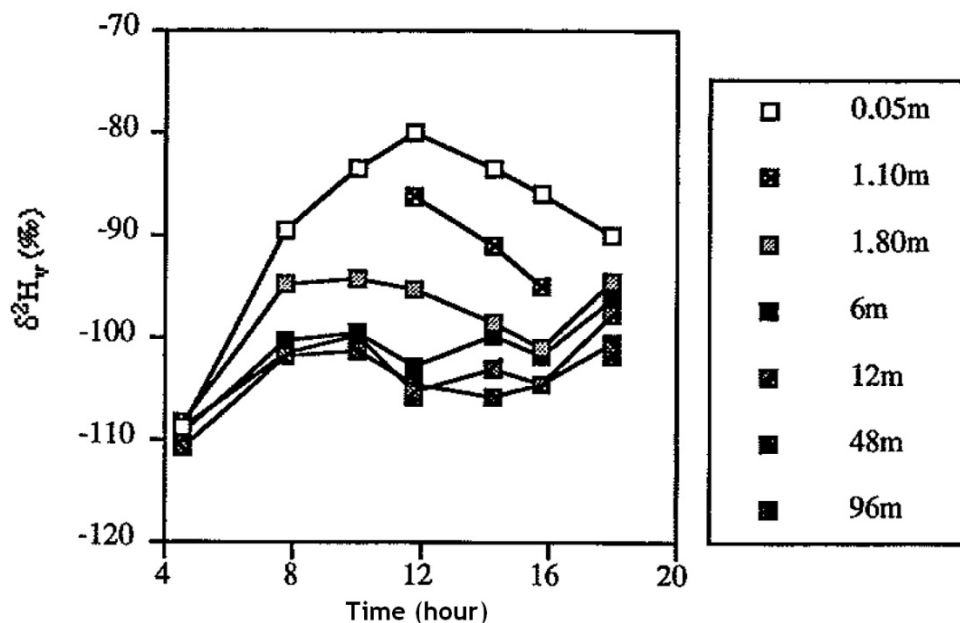
**Figure 15.** Comparative evolution of the oxygen-18 content in deuterium and the water vapor from transpiration and from water uptake by the roots (Bariac *et al.*, 1991).

### 6.2. Implications for the natural isotopic water cycle

The establishment of a specific isotopic signature for the water vapor transpiration goes through several stages:

- (1) Establishment of a permanent water regime in the sub-stomatal cavities of leaves and then of an isotopic steady state in the leaf water reservoir, then displacement of this steady state to another, during the day depending on environmental parameters.
- (2) Injection in the regional vapor of a water vapor coming from transpiration of the plant canopy. The average isotopic composition of this vapor measured at steady state remains identical to that of the

water of the plant collar, and therefore to the average, weighted by the root absorption, of the content of heavy water isotopes taken from the soil. So there is a natural isotopic labeling of the local vapor coming from the transpiration of the canopy (Figure 16).



**Figure 16.** Evolution of the deuterium content of the atmospheric water vapor that was sampled along a micrometeorological tower (96 m high) at the station of Villeau (Eure et Loir, France; Bariac *et al.*, 1990).

Under natural conditions, the specific isotopic composition of transpired water vapor will therefore allow to differentiate it from the vapor coming from the evaporation of water (Figure 17). Indeed, the atmospheric water vapor of oceanic origin gives rise to precipitation enriched in heavy isotopes through an isotopic fractionation factor at equilibrium that appears during condensation in the cloud, at the liquid-vapor interface. These rains infiltrate the ground and may be again concentrated in heavy isotopes through evaporation. There is no isotope discrimination during water absorption by roots. At the isotopic steady state, a leaf gives back to atmosphere a vapor whose isotopic composition is identical to that of the water taken up by the roots. The transpired vapor is necessarily more enriched in heavy isotopes than original ocean water vapor.

## 7. CONCLUSION

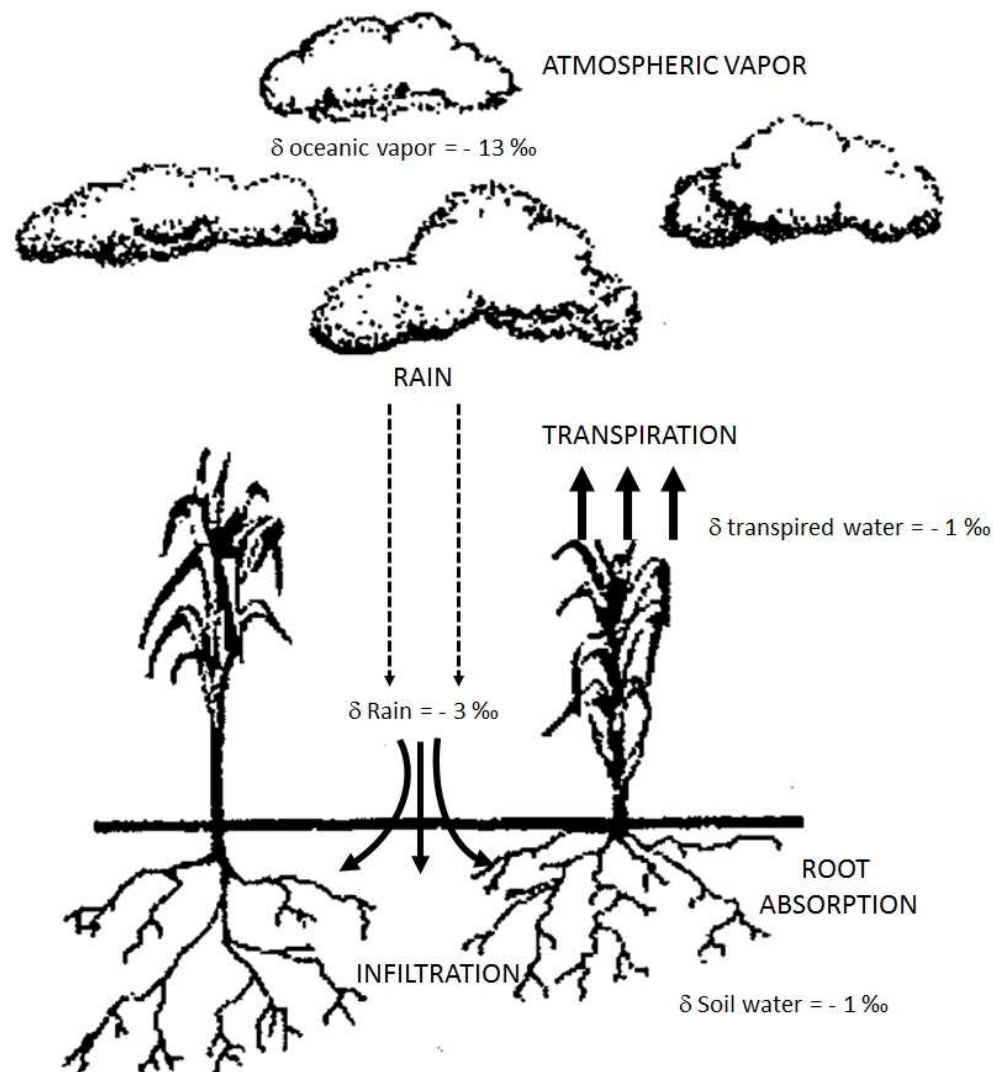
The need to determine the isotopic signal of water entering the continuum soil-plant-atmosphere appeared throughout the study. In fact, through this signal, we have:

- Addressed the water-soil-root relationship through the determination of the "average" depth of root absorption.
- Characterized an isotopic signature due to evaporation in some water samples of plant collar and therefore highlighted a root absorption in the surface layers of the soil.
- Characterized an isotopic signature related to rainfall in some water samples of plant collar and therefore highlighted a root absorption in the deeper soil layers. The sequence, to the scale of a circadian cycle, of isotopic signatures of water from the plant collar related to evaporation and

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precipitation, and finally to evaporation, suggests a differential mobilization of amounts of water present in the soil at different depths as a function of the evaporating request.

- Highlighted the existence of an elaborated sap (phloem sap) in the aerial organs involving little or no in transpiration and calculated the percentage of this sap compared to the xylem sap.
- Highlighted the existence of xylem sap in the leaves and calculate the percentage of this sap compared to the phloem sap.
- Calculated the isotopic composition of the output signal (= vapor transpiration) in the continuum soil-plant-atmosphere. It therefore becomes possible to differentiate the local vapor (canopy transpiration) from regional vapor (evaporation of the oceans).



**Figure 17.** Continental isotopic cycle of the water (Bariac *et al.*, 1987).

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