

## **The application of stable isotopes to study Biosphere-Atmosphere interactions in Mediterranean Forests Ecosystems**

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The terrestrial biosphere is a major component of the global carbon and water cycles. The biosphere can sequester carbon and, hence, can play a relevant role in mitigating the increase in CO<sub>2</sub> concentration in the atmosphere, mainly due to anthropogenic fossil fuel burning and deforestation. However, the biospheric sink capacity, especially in the Mediterranean area, is strongly dependent on water availability and this may become limiting because of exacerbated drought conditions due to global climate change.

Stable carbon and oxygen isotopes have become important tracers of CO<sub>2</sub> in the biosphere, as well as in the CO<sub>2</sub> exchange between the atmosphere and the biosphere. For example, using stable carbon isotope measurements one can distinguish the global carbon fluxes into individual components. Therefore, it is possible to determine what fraction of the CO<sub>2</sub> input to the atmosphere due to anthropogenic activities, that remains in the atmosphere, that absorbed by the oceans versus that absorbed by the land vegetation. In addition, C isotopes and isotopic partitioning among the major carbon cycle components provide powerful indicators of carbon isotopic composition of the atmosphere in present days, but also over the past 3-4 billion years. Stable oxygen and hydrogen isotopes are independent tracers to study the hydrological cycle and to separate fluxes into soil evaporation and vegetation transpiration. Stable isotopes in tree rings, ice cores and sediments represent natural records of plant ecophysiological responses and of paleoclimatic events. Stable oxygen isotopes are tracers of the equilibrium exchange between CO<sub>2</sub> and water in vegetation, soil and aquatic environment, while <sup>17</sup>O and <sup>18</sup>O can be used to assess the biosphere productivity.

While much information has accumulated on stable isotope processes at the single plant level on one hand, and at the global scale on the other, major questions remain on the processes at the ecosystem level.

The ecosystem CO<sub>2</sub> and water vapour exchange can be measured with the eddy covariance methodology, but it cannot provide information about individual flux components. Eddy covariance together with stable isotope analysis can provide both quantitative and qualitative data on single ecosystem components. Photosynthetic and respiratory fluxes differ in their carbon isotope composition ( $\delta^{13}\text{C}$ ) and influence the isotopic composition of atmospheric CO<sub>2</sub> within the canopy

boundary layer. Discrimination against  $^{13}\text{C}$  during photosynthesis is well understood, while recent evidence point to a significant discrimination during respiration. However, variation of photosynthetic carbon isotope discrimination ( $\Delta$ ) can be caused by environmental stresses such as drought, salinity and temperature variation. This, if not properly taken into account, can lead to misinterpretation of atmospheric  $\text{CO}_2$  isotopic signals. For example, global or regional scale variations in  $\Delta$  induced by drought stress or ENSO (El Niño-Southern Oscillation)-related changes in  $\text{C}_3/\text{C}_4$  productivity can cause variations in atmospheric  $^{13}\text{CO}_2$  that could erroneously be interpreted as a shift in the magnitude of the terrestrial carbon sink rather than a shift in  $\Delta$ .

Stable isotope composition of photosynthetic carbohydrates (e.g., sucrose and starch) proven to be accurate indicator of photosynthetic  $\Delta$ , which, in turn, depends on environmental conditions influencing stomatal conductance and intercellular  $\text{CO}_2$  concentration. Since these carbohydrates are the putative respiratory substrate, the analysis of their isotopic composition compared to that of canopy  $\text{CO}_2$  allow partitioning of photosynthetic and respiratory fluxes and to estimate the sink capacity of vegetation. Therefore, the analysis of stable isotopes in plant carbohydrates are proposed as tracers of photosynthetic productivity and sink capacity in terrestrial biosphere.

Also higher plant leaf waxes have isotopic composition depending on photosynthetic discrimination and, hence, record an integrated short-term isotopic signal. Ablated leaf waxes transported in continental aerosols appear to record a large spatially integrated signal of photosynthetic  $\Delta$ . Therefore, strategically located measurements of wax aerosols may be used to produce direct regional scale data on spatial and temporal variations in  $\Delta$  that can be incorporated into models to improve estimates of the magnitude and geographical pattern of carbon sinks.

The availability of new analytical techniques has increased the interest in using  $^{18}\text{O}/^{16}\text{O}$  and D/H ratios both as tracers of the movement of water along the soil-plant-atmosphere continuum, and as integrative indicators of microclimatic conditions and physiological processes related to water-use by plants. Leaf water is generally enriched in the heavier isotopes with respect to xylem water because of transpiratory enrichment, while xylem water reflects the isotopic signature of soil water taken up by plants. The extent of the isotopic enrichment in leaf water relative to soil water depends on both atmospheric conditions and stomatal regulation of water loss. Particularly, leaf isotope enrichment is affected by leaf- and air-vapour pressures, which are dependent on leaf and air temperatures, the fraction of evaporating water to source water and their mixing to compose the bulk leaf water, the isotopic composition of atmospheric water vapour and stomatal and boundary layer resistances to water vapour diffusion. The leaf water enrichment during transpiration has been modelled adapting the process of evaporative enrichment from a free water body (e.g. lake). It should be noted here that the isotope fractionation occurs in a precise pool of the leaf water called evaporating water; this is the fraction of leaf water at the sites of transpiration. In contrast, bulk leaf

water is all of the water pools present in the leaf. The variation in the oxygen isotope compositions of soil, xylem and leaf water and vapour surrounding the leaf has the potential to be a relevant signal of plant-environment interactions and adaptive processes.

The potential use of the above applications and some case studies on stable isotopes are discussed.