

First field record of ^{17}O -excess of atmospheric vapor measured by cavity ring-down spectroscopy

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Triple oxygen isotope data (expressed by ^{17}O -excess) provide a constraint on kinetic fractionation effects and mixing processes in the water cycle, complementing the classical d-excess. However, high-precision triple oxygen isotope analyses of atmospheric water vapor are challenging and remain scarce. Here, we present the first field record of simultaneous measurements of triple oxygen and hydrogen isotope ratios of atmospheric water vapor using a cavity ring-down spectrometer (Picarro L2140-i).

Measurements of atmospheric water vapor have been carried out in the French Mediterranean at the 'O₃HP' platform at the Upper-Provence Observatory since December 2020, at different heights below and above the Downy oak forest canopy. The calibration is performed on a weekly basis using two liquid water standards vaporized at various mixing ratios covering the local range of atmospheric water vapor concentrations (3000-15000 ppmv). A thorough examination of the mixing ratio dependency of atmospheric water vapor measurements was carried out in order to develop a calibration protocol enabling high-precision analyses of ^{17}O -excess and d-excess in atmospheric water vapor. Monte Carlo simulations suggest an uncertainty of calibrated atmospheric water vapor data of 0.3 ‰, 0.5 ‰, 4.0 ‰, 11 per meg, 0.8 ‰ for $\delta^{17}\text{O}$, $\delta^{18}\text{O}$, $\delta^2\text{H}$, ^{17}O -excess, and d-excess, respectively, for atmospheric water vapor concentrations >5000 ppmv.

On a scale of several days, the $\delta^{18}\text{O}$ of atmospheric water vapor above the forest canopy varies by 20 ‰. $\delta^{18}\text{O}$ values increase with the atmospheric water vapor concentration. The d-excess variations are within the range of 20 ‰. Variations in ^{17}O -excess are generally in the order 30 per meg, but can exceptionally reach 60 per meg. The d-excess is anticorrelated with $\delta^{18}\text{O}$, while no correlation is observed between ^{17}O -excess and $\delta^{18}\text{O}$. The temporal dynamics of the isotopic composition of atmospheric water vapor will be related to regional meteorological conditions, air mass sources and transport processes, as well as local effects induced by precipitation and evapotranspiration, in order to determine the main factors influencing the isotopic composition of atmospheric water vapor at the study site. In particular, comparison of ^{17}O -excess and d-excess will give insight into their combined potential for