The isotopic composition of water vapor: from discrete to continuous measurements. A focus on calibration methods

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The water residence time in the atmosphere is approximately nine days, the shortest residence time in any major reservoir of the whole water cycle on the planet. Nevertheless, water vapor is a key factor in climate and hydrology due to its dynamic behavior. The isotopic composition of water vapor can highlight several processes of the water cycle that link the water reservoirs to the atmosphere (Galewsky et al., 2016). In the past, the isotopic composition of water vapor was generally inferred from precipitation data, assuming isotopic equilibrium between rain and water vapor. This assumption works well when precipitation is abundant but gives misleading results when precipitation is scarce. A common method to determine the isotopic composition of water vapor is the cryotrapping technique, proposed by Craig et al., (1963). Cryotrapping consists in freezing all the moisture content of the air (to avoid fractionation) and analyze the liquid sample with the regular mass spectrometry technique. This process includes the designing of customized cold traps and usually requires several man-hours due to the long sampling time (2 - 8 hours per sample). With the advent of the laser absorption spectrometry (LAS) technique is now possible to determine the isotopic composition of water vapor with sampling time down to seconds. This novel technique increases our knowledge about the isotopic composition of water vapor and gives a substantial help in our understanding of the water cycle, both on global and local scales. However, the continuous measurement of isotopic composition of water vapor requires a specific method to calibrate the large amount of data resulting as the output of a Cavity Ring-Down Spectroscopy (CRDS) analyzer. This includes the production of vapor with known isotopic composition, determination of the response of the analyzer to different humidity levels and correction of the instrumental drift. In this work, we present a summary of potential calibration techniques for continuous measurements of the isotopic composition of water vapor. The study goes in-depth on the developing of a customized calibration unit for a commercial CRDS analyzer (Picarro L1102i). Continuous measurements will be compared to water vapor samples collected with cryotraps and several continuous measurements will be presented highlighting sub-daily processes in the atmospheric boundary layer.

References:

Craig, Harmon, L. I. Gordon, and Y. Horibe. "Isotopic exchange effects in the evaporation of water: 1. Low-temperature experimental results." Journal of Geophysical Research (1963).

Galewsky, Joseph, et al. "Stable isotopes in atmospheric water vapor and applications to the hydrologic cycle." Reviews of Geophysics (2016).