Geophysical Research Abstracts
Vol. 16, EGU2014-14973, 2014
EGU General Assembly 2014

Measuring water vapor isotopes using Cavity Ring-Down Spectroscopy: improving data quality by understanding systematic errors and calibration techniques

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The stable isotopes of hydrogen and oxygen in water are commonly used to understand the present day hydrological cycle and reconstruct climates of the geologic past. Water vapor isotopes are also increasingly used to probe atmospheric dynamics, including the connection between tropical convection and polar precipitation, stratospheric intrusions of water vapor, boundary layer mixing and cloud formation [e.g., 1, 2, 3]. By utilizing this information, it is now possible to incorporate water isotopes into atmosphere-ocean general circulation models (AOGCMs) as a tool for generating "transfer functions" between a climate variable and its associated isotopic signal [4]. In so doing, we will improve our understanding of how, for example, water isotopes in polar or high-altitude ice cores and the oxygen isotopic composition of terrestrial carbonates are related to global or regional temperature change, seasonality in precipitation, or the intensity of precipitation, among other variables. However, these model-derived functions are only as good as the data, and parameterizations, that go into the models.

Over the past five to ten years, the advent of commercially-available laser-based technologies, such as Cavity Ring-Down Spectroscopy (CRDS), has transformed the ease by which water isotopes are measured. This is particularly true for studies of ambient water vapor which are ideally-suited to the continuous flow capacity of CRDS analyzers. Measuring water vapor isotopes by CRDS requires no pre-treatment, discrete sampling or cryogenic trapping; instead water vapor isotopes can be measured in-situ to a high precision. For example, the Picarro L2130-i has a precision, defined as the standard deviation of 100-second average measurements, of better than 0.04 per mil and 0.1 per mil for d18O and dD at 12,500 ppm water vapor concentration, respectively. As a result, the quantity of water vapor isotope data has increased substantially. As with any analytical technique, challenges do exist when making ambient water vapor isotope measurements via CRDS and these should be addressed to ensure data integrity.

Here we review a number of systematic errors introduced when making ambient water vapor measurements using CRDS, and where appropriate, provide suggestions for how to correct for them. These include: the dependence of reported delta values on water vapor concentration, the interference of CH4 on water spectra, achieving reliable low humidity measurements ($[H_2O] < 5{,}000$ ppm), and calibration for both absolute accuracy and instrument drift. We will also demonstrate the relationship between calibration frequency and precision, and make recommendations for ongoing calibration and maintenance. Our aim is to improve the quality of data collected and support the continued use of water vapor isotope measurements by the research community.

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