



On the cross-sensitivity between water vapor mixing ratio and stable isotope measurements of in-situ analyzers

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In recent years there has been an increasing amount of water vapor stable isotope data collected using in-situ instrumentation. A number of papers have characterized the performance of these in-situ analyzers and suggested methods for calibrating raw measurements. The cross-sensitivity of the isotopic measurements on the mixing ratio has been shown to be a major uncertainty and a variety of techniques have been suggested to characterize this inaccuracy. However, most of these are based on relating isotopic ratios to water vapor mixing ratios from in-situ analyzers when the mixing ratio is varied and the isotopic composition kept constant. An additional correction for the span of the isotopic ratio scale is then applied by measuring different isotopic standards. Here we argue that the water vapor cross-sensitivity arises from different instrument responses (span and offset) of the parent H_2O isotope and the heavier isotopes, rather than spectral overlap that could cause a true variation in the isotopic ratio with mixing ratio. This is especially relevant for commercial laser optical instruments where absorption lines are well resolved. Thus, the cross-sensitivity determined using more conventional techniques is dependent on the isotopic ratio of the standard used for the characterization, although errors are expected to be small. Consequently, the cross-sensitivity should be determined by characterizing the span and zero offset of each isotope mixing ratio. In fact, this technique makes the span correction for the isotopic ratio redundant. In this work we model the impact of changes in the span and offset of the heavy and light isotopes and illustrate the impact on the cross-sensitivity of the isotopic ratios on water vapor. This clearly shows the importance of determining the zero offset for the two isotopes. The cross-sensitivity of the isotopic ratios on water vapor is then characterized by determining the instrument response for the individual isotopes for a number of different in-situ analyzers that employ different optical methods. We compare this simplified calibration technique to more conventional characterization of both the cross-sensitivity determined in isotopic ratio space and the isotopic ratio span. Utilizing this simplified calibration approach with improved software control can lead to a significant reduction in time spent calibrating in-situ instrumentation or enable an increase in calibration frequency as required to minimize measurement uncertainty.