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*Supplement of*

## **Detection and variability of combustion-derived vapor in an urban basin**

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## Supplement

### **Supplemental Information on the Cavity Humidity Correction for the Picarro L2130-i**

Laser-based isotope ratio cavity ringdown spectrometers exhibit an apparent isotopic bias that varies with cavity humidity (Aemisegger et al., 2012; Schmidt et al., 2010; Sturm and Knohl, 2009). Calibration of ambient humidity measurements to the common VSMOW-VSLAP scale therefore requires an estimate of this apparent dependence of isotopic composition depending on humidity. This bias is thought to arise from two sources: 1) nonlinearities arising from variability in the spectrometer electronics and software calibration routines at different cavity mixing ratios and through time (e.g., Aemisegger et al., 2012) and 2) for measurements of standard waters, vapor introduced into the cavity often represents a mixture between standard waters and fugitive vapor from the dry gas source (e.g., Aemisegger et al., 2012; Gorski et al., 2015). In theory, the latter source of error can be corrected using an isotopic mixing model so long as a reasonable estimate for the amount and isotopic composition of the fugitive vapor can be determined. Gorski et al. (2015) assumed that 250 ppm of vapor exited the Drierite drying column without fractionation, and therefore the isotopic composition of this fugitive vapor was simply assumed to be a time-averaged mean prior to measurement of the standard. We have not used this assumption here, and no attempt at a “dry-gas” correction has been attempted, as neither the amount or the fractionation of vapor passing through the Drierite column is known. Aemisegger et al. (2012) reached a similar conclusion, leaving the potential for these calibrations to be improved in the future if the amount of water vapor exiting the column and degree of fractionation through the column, and their variance through time as the drying agent is consumed, can be quantified.

We characterize the apparent bias in isotopic composition with cavity humidity by varying the rate of standard water injection into the Picarro Standards Delivery Module. The

same Picarro L2130-i water vapor isotope analyzer was used throughout the experiment (SN: 1175HIDS2045). We performed this calibration four times during the UOU period of record (POR) on this analyzer: (a) December 2013, (b) June 2014, (c) February 2017, and (d) July 2017. The analyzer has continued to operate at UOU after the POR used for this study; therefore, we include a fifth calibration performed in April 2018. Water vapor mixing ratios were varied from 1,000 ppm to 35,000 ppm. As these calibrations were performed irregularly in time, we pool all of them into one correction equation in order to sample the full variance of this bias through time. The isotopic bias is calculated as a deviation from the mean standard value measured at humidities between 15,000 and 25,000 ppm, where there is little change in apparent isotopic composition with humidity and contains the humidity range at which laboratory standard waters were calibrated. In order to give all humidity values comparable standing in the regression, data were sorted into humidity bins spanning 500 ppm and a mean and standard deviation value calculated for each bin. The resulting data exhibits an isotopic bias proportional to  $1/[H_2O]$ ; therefore an equation describing this bias correction was estimated using Deming regression, which accounts for uncertainty in both the independent and dependent variables. Best fit slope and intercept values, as well as values corresponding to 95% confidence intervals, were estimated for both  $\Delta^{18}O$  and  $\Delta^2H$ , and these best fit equations are listed below ( $H_2O$  given in ppm):

$$\Delta^{18}O_{\text{offset}} = 0.308 - 5838.95/[H_2O]. \text{ (best fit)}$$

$$\Delta^{18}O_{\text{offset}} = 0.424 - 4188.57/[H_2O]. \text{ (upper 95\% CI)}$$

$$\Delta^{18}O_{\text{offset}} = 0.193 - 7489.32/[H_2O]. \text{ (lower 95\% CI)}$$

$$\Delta^2H_{\text{offset}} = 0.408 - 9726.72/[H_2O]. \text{ (best fit)}$$

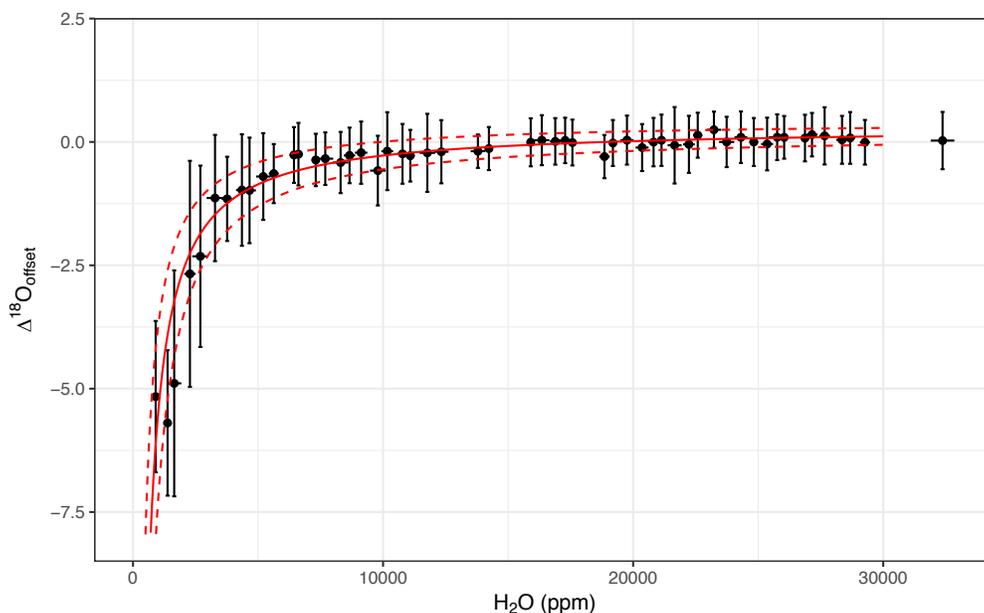
$$\Delta^2H_{\text{offset}} = 0.794 - 2894.36/[H_2O]. \text{ (upper 95\% CI)}$$

$$\Delta^2H_{\text{offset}} = 0.023 - 16559.08/[H_2O]. \text{ (lower 95\% CI)}$$

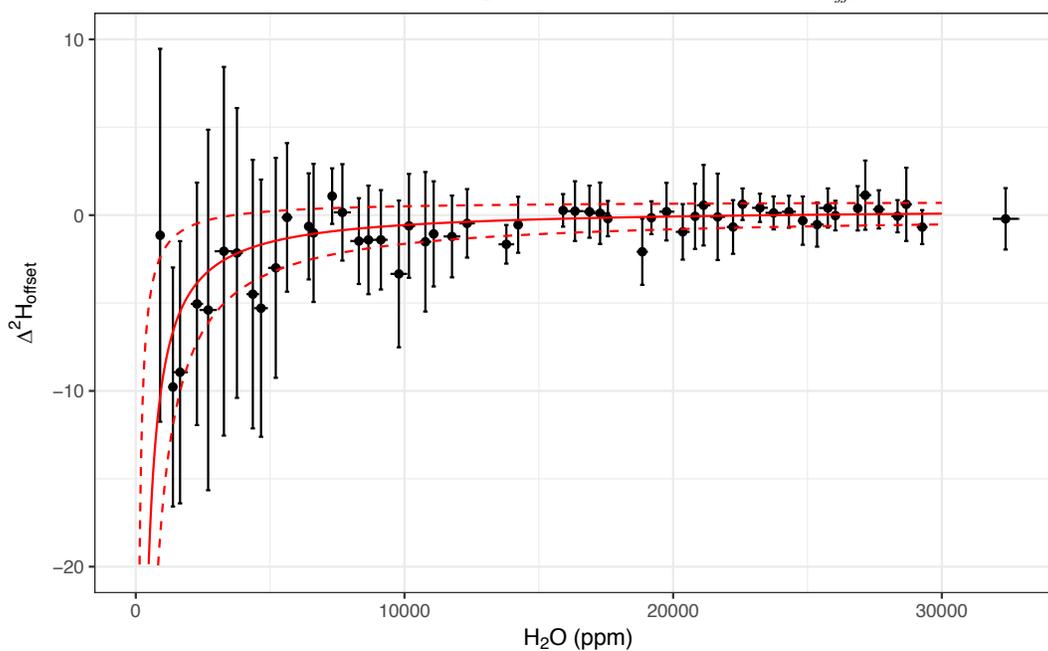
Observed isotopic compositions were corrected for these apparent biases by subtracting the appropriate offset values from the observed isotopic composition using the calculated offset for that humidity value:

$$\delta X_{\text{humidity corrected}} = \delta X_{\text{measured}} - \Delta X_{\text{offset}}(\text{humidity})$$

The apparent deviation in isotopic composition with humidity for both oxygen (Fig. S1) and hydrogen (Fig. S2), along with these best-fit regressions and confidence intervals.

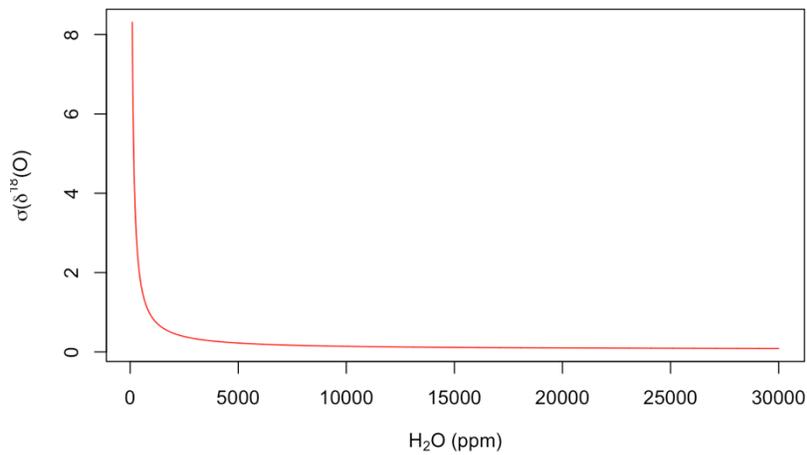


*Fig. S1. Correction equation and data for  $\Delta^{18}O_{\text{offset}}$ , with 95% confidence intervals shown for each humidity bin and for the correction equation. Regression is weighted using errors associated with both  $H_2O$  concentration and  $\Delta^{18}O_{\text{offset}}$ .*

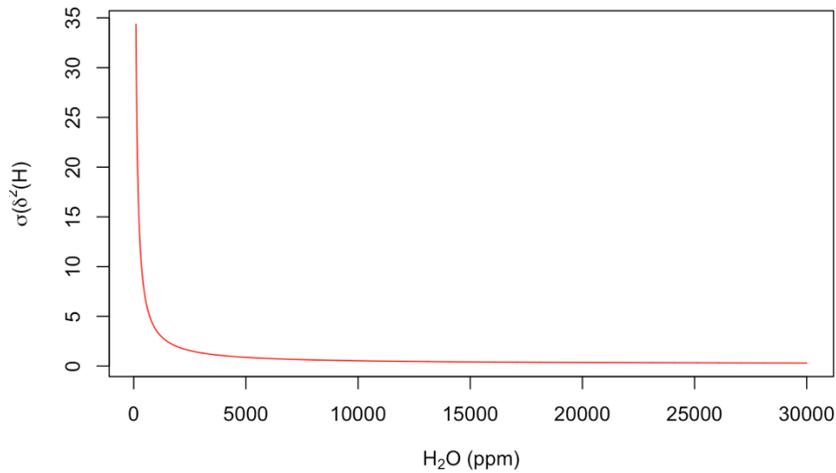


*Fig. S2. Correction equation and data for  $\Delta^2H_{\text{offset}}$ , with 95% confidence intervals shown for each humidity bin and for the correction equation. Regression is weighted using errors associated with both  $H_2O$  concentration and  $\Delta^2H_{\text{offset}}$ .*

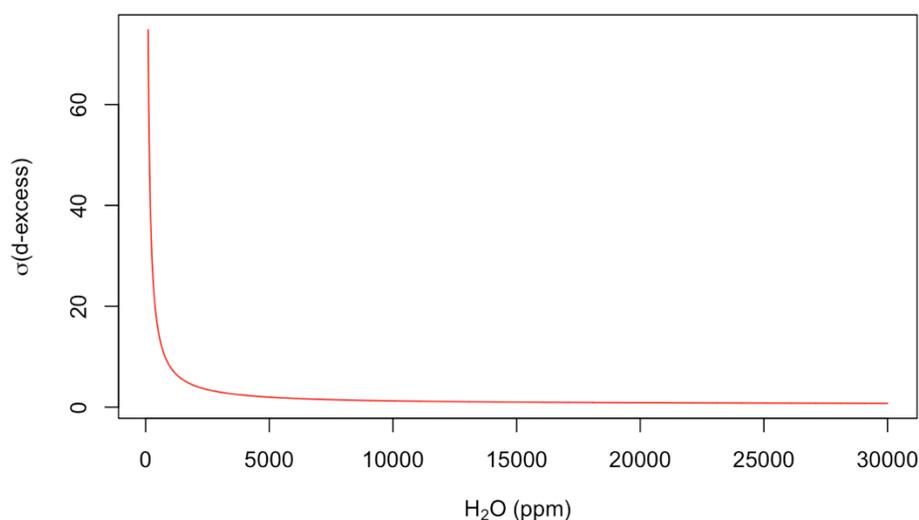
The 95% confidence intervals on these regressions was used to generate an uncertainty estimate across all of these tested humidity levels. Plots of estimated standard deviation against cavity humidity are shown for  $\delta^{18}\text{O}$  (Fig. S3),  $\delta^2\text{H}$  (Fig. S4), and d-excess (Fig. S5), assuming errors in  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$  are independent. This uncertainty is considered to be the dominant source of uncertainty in our isotopic measurements, as: (a) calibration of standards are subject to the same relationship, and (b) two-point calibrations during the period of record tend to be highly linear with an  $R^2$  value very close to 1, and therefore do not contribute significant additional uncertainty.



*Fig. S3. Estimated 1-sigma uncertainty in  $\delta^{18}\text{O}$  as a function of humidity.*



*Fig. S4. Estimated 1-sigma uncertainty in  $\delta^2\text{H}$  as a function of humidity.*



*Fig. S5. Estimated 1-sigma uncertainty in d-excess as a function of humidity.*

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