

## ***Interactive comment on “Flux correction for closed-path laser spectrometers without internal water vapor measurements” by R. V. Hiller et al.***

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Received and published: 6 March 2012

Review: R.V. Hiller, et al., Flux correction for closed-path laser spectrometers without internal water vapor measurements. MS No.: amt-2011-204 MS type: Research Article

### General Comments

This paper addresses an important issue for users of LGR methane analyzers that do not measure water vapor. The need for appropriate spectral corrections and dilution corrections due to the effects of water vapor on other gases being measured is well known. In closed path instruments these corrections must be made on the basis of the actual contemporaneous water vapor concentration in the optical cell at the instant the scalar of interest is being measured. This is straightforward if the instrument mea-

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asures water vapor simultaneously with the scalar of interest; however, if water vapor is only measured in the open air with an LI-7500 Open Path CO<sub>2</sub>/H<sub>2</sub>O analyzer, for example, this becomes a much more complicated problem because tube delays, tube attenuation of H<sub>2</sub>O fluctuation amplitudes, and relative humidity effects must also be taken into account. In general, this paper does a nice job of delineating these phenomena, describing their physical basis, and providing appropriate corrections for them. I will mention several areas for the author's further consideration in my "Specific Comments," but none of them threaten the overall conclusions of the paper.

### Specific Comments

1. I now turn to a more general issue that confounds this paper to a small degree and has wider implications. The issue concerns the concept of dry mole fraction. This concept is both necessary and sensible for scalars other than water vapor. In humid air, it expresses the mole fraction of a scalar other than water vapor (e.g. CO<sub>2</sub> or CH<sub>4</sub>) after water vapor is removed. In practice, if the mole fraction (or other concentration unit) of a scalar is measured in humid air, and if the water vapor is then removed and the gas is measured again, the measured result will give dry mole fraction, assuming instrument calibrations are correct. This concept is important in all types of flux measurements where a flow rate (e.g. chamber measurements) or a wind speed (e.g. open air fluxes) is augmented in one direction by the addition of a third component, in this case water vapor; and it is also important when scalar concentration measurements are perturbed by the addition or removal of water vapor at constant pressure. We call this a dilution effect. Since water vapor is the only additional component whose concentration varies over a sufficiently large range to make a quantitative difference, we routinely correct to dry conditions to remove the water vapor dilution effect, but neglect the dilution effect for the variation of other gaseous components. The important point here is that a dilution correction is needed only when an additional component is added to the mixture other than the component being measured.

So what are the consequences if we apply the concept of "dry mole fraction" to water

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vapor itself? A “dry mole fraction” would then represent the mole fraction of water vapor in air that contains no water vapor. Clearly, dry mole fraction of water vapor does not exist as a physical entity; it is simply a computed ratio of the number density (or mass density) of water molecules relative to non-water molecules in a gaseous mixture. I respectfully suggest that such a concept is both unnecessary and misleading, at least as it relates to instrument spectral effects, calibrations, and dilutions. Arguably, that may be true in other contexts as well, but that broad question is beyond the scope of this review.

To pursue this further and consider its consequences for this paper, we have,

$$1 = x_a + x_s + x_w, (1)$$

where the  $x_i$  are the mole fractions of dry air (a), scalar (s), and water vapor (w). Along with the ideal gas law, this expression can be recast as a sum of partial pressures, number densities, or absolute numbers of molecules. In all cases, it expresses conservation of mass, and in terms of partial pressures, it gives Dalton’s law of partial pressures. To obtain an expression for dry mole fraction of non-water components we simply subtract  $x_w$  from both sides of the equation and divide by  $1-x_w$  to obtain,

$$1 = x_a/(1-x_w) + x_s/(1-x_w) = x_{da} + x_{ds}, (2)$$

where  $x_{da}$  is the mole fraction of dry air and  $x_{ds}$  is the dry mole fraction of scalar. Like equation (1), equation (2) includes the effect of water vapor, it is completely general, and it conserves mass. If we physically remove the water vapor from a parcel of moist air that is described by equation (1), the mole fractions of the resulting parcel of dry air will be described by equation (2) and Dalton’s law applies to both gases. Thus, the dry mole fractions described by equation (2) represent physical entities that can be generated and measured.

By contrast, the “dry mole fraction of water vapor” is an arbitrary ratio that cannot be physically produced. Consider the implications of this concept. We might write,

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$$1/(1-x_w) = x_a/(1-x_w) + x_s/(1-x_w) + x_w/(1-x_w),$$

$$1/(1-x_w) = x_{da} + x_{ds} + x_{dw} \text{ and } (3)$$

$$1/(1-x_w) > 1 \text{ for all } x_w > 0,$$

where,  $x_{dw}$  is the water vapor dry mole fraction. But now, the sum of mole fractions adds to a number greater than one. The concept of mole fraction is undermined and mass is not conserved if “mole fractions” are thought to sum to unity. Unlike equations (1) and (2), partial pressures computed from “mole fractions” in equation (3) would not sum to total pressure, but to an artificially increased “pressure” that does not physically exist.

Describing real processes in terms of physically unrealistic variables has undesirable consequences. Suppose we challenge a hypothetical gas analyzer that is assumed to be perfectly linear in its response with a series of increasing water vapor mole fractions. At constant temperature and pressure, the only variable leading to a change in absorption will be the number of water molecules in the optical path as specified by the increasing water vapor mole fraction. If the instrument is calibrated in mole fraction units and its output is plotted against the actual water vapor mole fractions provided, the resulting plot will be a straight line with a slope of unity and intercept of zero. Now suppose the same instrument output is plotted instead against “water vapor dry mole fraction”, which is the actual mole fraction divided by  $1-x_w$ . The error introduced by dividing by  $1-x_w$  will become increasingly large as  $x_w$  increases and the true water vapor mole fraction on the y-axis will become increasingly over-estimated. The plot will become increasingly non-linear and have slight upward curvature; if a linear regression is performed the slope will be greater than one and the intercept will be less than zero, as the authors found when they did this experiment (Tables 1 and 2). Thus, one immediate consequence of using units of water vapor dry mole fraction during water vapor calibration is that it will make a linear instrument appear non-linear, or have a non-ideal slope and intercept, if linear calibration is used.

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The same kind of unnecessary errors can be expected for other physical processes. For example, both dilution and spectral broadening by water vapor depend upon the actual mole fraction (or number density, or partial pressure at constant T and P) of water vapor in the gas. Therefore, expressing these effects in terms of an artificial entity such as “water vapor dry mole fraction” will inevitably lead to unnecessary errors. For example, it is likely that the use of this variable contributed to the non-linearity observed in equation (10). Fortunately, the errors are modest and vary in a smooth and predictable way. In this and cited papers, the dilution plus spectral broadening effects were compensated by an empirical regression equation so the errors were undoubtedly subsumed into the regression coefficients (Tables 1 and 2). Consequently, after taking these steps, the empirical effects on the final results might be negligible. The same is true of the calibration example cited above. This is fortunate, but it does not justify the use of an artificial variable that generates unnecessary errors.

To conclude this point, I believe the overall approaches the authors used to correct for the effects of water vapor on methane flux measurements, were generally clearly presented and correct; however, along the way they, like others before them, used the notion of “water vapor dry mole fraction”, which I have shown leads to both theoretical and practical problems. Fortunately, the regression methods used minimized errors in the final results (Figure 1) and probably did not invalidate their results or conclusions. Since the authors took pains to estimate errors resulting from their methods, I do not suggest their results be recomputed with true mole fraction, although it would have been better if they had done that from the beginning; however, this topic does merit some mention in the Discussion.

I suggest the use of “water vapor dry mole fraction” should be avoided as a unit for gas analyzer calibration because (1) it distorts quantitative understanding of the response of physical processes to water vapor, (2) it does not conserve mass or support Dalton’s law when mole fractions are summed to unity, (3) it implies a dilution correction where no dilution correction is needed; and (4), inasmuch as it represents “the mole fraction of

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water vapor in air that contains no water vapor,” it is not conceptually clear or physically attainable, except at  $x_w = 0$ .

2. In several places in the manuscript phrases appear such as, “the observed flux in the cell” (p.368 line 13), or “(w’H<sub>2</sub>O)<sub>over-bar</sub> observed in the measurement cell” (p.368 line 10), or similar phrases (e.g. p.369 line 25, p. 371, line 2). It is reasonably clear what the authors mean, but it is also true that water vapor flux is not observed “in” the measurement cell. If that were the case, we would be focusing on movement of water vapor through the cell, not on LE at the tower. Instead, water vapor fluctuations (H<sub>2</sub>O) are observed in the measurement cell from which water vapor fluxes are computed. I suggest that wording in the affected places be adjusted to reflect this more precise description.

#### Technical Comments

p. 354 line 18. Add a comma following FMA.

p. 356 line 3. Change “measurements was” to “measurements were”.

p. 356 line 10. Change “heat relatet” to “heat-related”.

p. 356 line 11. “evindence” to “evidence”.

p. 356 line 18. Change to something like, “Therefore, the water vapor dilution and gas temperature fluctuations in the cell define the magnitude of the WPL correction.”

p. 356 line 23. “density effects...is...” to “density effects...are...”.

p. 357 line 23. Change, “H<sub>2</sub>O is also only measured by the FGGA, but retrieved from the same laser absorption spectrum as CH<sub>4</sub>” to, “H<sub>2</sub>O is also only measured by the FGGA, but the same laser used to measure CH<sub>4</sub> is tuned to a nearby H<sub>2</sub>O absorption line.”

p. 364 line 26. “by” to “be”.

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p. 366 line 1. “The variability of the  $(w'H_2O)_{\text{over-bar}}$  parallel increases with increasing L. Please clarify this statement. The meaning is not clear.

p. 366 line 25. “diverted” to “diverged”

p. 368, line 16 says, “E in Eq. (13) was divided by the calculated damping effect d (Eq. 11) to simulate. . .” Equation 11 computes the damping factor L. The quoted line implies E should be divided directly by L. But the previous sentence says “. . .the damping effect is assessed according to Eqs. (4) or (5). . .”, which contain L. This is confusing. Please clarify the definition of d in Eq. (13).

p. 369 line 15. “inbetween” to “in between”. p. 369 line 24. “The water vapor flux is damped by the measurement system and hence is reduced in the cell.” to “The water vapor frequency response is damped by the measurement system so the flux computed from H<sub>2</sub>O' in the cell is reduced.”

p. 371 line 2. “While damping reduces  $(w'H_2O)_{\text{over-bar}}$  observed in the cell, the cross-sensitivity effects. . .” to “While damping reduces H<sub>2</sub>O' observed in the cell, . . .”

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Interactive comment on Atmos. Meas. Tech. Discuss., 5, 351, 2012.