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COMMENT ON "AN ALTERNATIVE APPROACH FOR CO_2 FLUX CORRECTION CAUSED BY HEAT AND WATER VAPOUR TRANSFER" BY LIU

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The need and methodology to correct open-path eddy covariance estimates and determine surface exchange were documented in a landmark article a quarter of a century ago (Webb et al., 1980). Interest in these 'Webb corrections' is increasing, as seen in both their widespread application and recent articles re-examining their use (Paw U et al., 2000; Fuehrer and Friehe, 2002; Liebethal and Foken, 2003). Indeed, hundreds of eddy covariance tower sites now form a global network (Baldocchi et al., 2001), many employing open-path sensors to measure CO_2 and water vapour densities. Regrettably, the recent article of Liu (2005) represents a flawed interpretation, of both the basic equation of state and the Webb corrections, whose publication obscures the open-path correction issue.

The essential first step in deriving the Webb corrections is to define an equation of state for turbulent perturbations. This can take various forms including those shown by Equation (9b) of Webb et al., (1980), and Equations (4) and (6) of Liu (2005). To demonstrate clearly Liu's error in interpretation, the perturbation equation of state is reproduced here in the form most relevant to the correction of open-path eddy covariance.

Open-path gas analysers detect extinction targets in a constant sensing volume, and thus respond to molar density (n). Partitioning the molar density of air ($n = n_v + n_a$) yields components representing water vapour (n_v) and all other gases ('dry air', n_a) including trace amounts of CO_2 (n_c). In molar density terms, Equation (4) of Liu (2005) may be simplified to an equally valid expression of the perturbation equation of state

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$$n'_a + n'_v = -\frac{P}{R\overline{\overline{T}}^2}T'. \tag{1}$$

This is the expansion/compression equation: for a given population of molecules (i.e., a parcel), the total volume occupied varies according to fluctuations in temperature. Due to partitioning of n' into components n_v and n_a, Equation (1) may be viewed as describing two ideal gases competing to occupy a temperature-dependent volume. In such a three-term balance, perturbations in any one term can induce changes in the other two. Given that this perturbation equation of state for total moist air underpins the derivation of the Webb corrections, Liu is mistaken in the assertion that Webb et al. (1980) accounted for 'the effects of expansion/compression of the dry air … ignoring the water vapour part'.

The fundamental assumption underlying the Webb corrections – that the surface is neither a source nor sink of dry air – is likewise misinterpreted by Liu. This appropriate boundary condition does not at all imply that 'the mean vertical velocity results only from the expansion/compression of the dry air (not the total moist air)' Rather, when combined with the decomposition of the dry air flux into mean and fluctuating contributions, the boundary condition merely provides a diagnostic equation for mean vertical velocity over an ideal surface. It is equally valid in dry and humid environments, independent of water vapour transfer. As stated above, expansion/compression of all air (dry air and water vapour) is governed by Equation (1).

Having misconstrued, to my mind, the fundamentals of the Webb corrections, the Liu (2005) derivation then proceeds in an independent direction. The equation of state is expressed in terms of specific volume, but the derivation goes awry. Liu's Equation (11) is an incorrect formulation suggesting that expansion-induced changes in CO_2 density depend directly on specific volume, and is reproduced here for illustrative purposes

$$\rho'_{CO_2\,\mathrm{exp}} = -\rho_c\frac{V'}{\overline{\overline{V}}}. \quad \text{(2; Equation (11) of Liu, 2005)}$$

A simple thought experiment reveals its deficiency: replacing any number of nitrogen molecules with an equal number of water vapour molecules clearly changes specific volume but affects neither CO_2 density nor expansion/compression. Stated otherwise, the density of a given constituent gas does not depend on the molecular mass of its neighbour molecules. Liu's Equation (10) is analogous for the case of water vapour, and likewise invalid. Rather, water vapour density perturbations are defined correctly by Equation (1), including the effects of expansion/compression.

The derivation by Liu (2005) then substitutes the invalid Equations (10) and (11) back into the equation of state to derive erroneous corrections as an alternative to those of Webb et al. (1980). With the exception of the reproduced Webb corrections, all subsequent equations in the main text of Liu (2005) are in error, and the conclusions dubious.

The appendix to Liu's article also contains significant errors and further demonstrates the inadequacy of the proposed corrections. Most egregiously, Equation (A8) is a patently erroneous expression of the CO_2 flux unless the final term (which Liu equates with the proposed corrections) is identically zero. The fact that Equations (A9) and (19) are identical may be attributed to unfortunate coincidence, since they are incorrect for independent reasons.

A final and hopefully instructive remark concerns the title chosen by Webb et al. (1980) to describe corrections 'for density effects' which may lead to confusion. Again, Equation (1) provides the framework for two effects that influence n_a (and hence n_c as measured by the gas analyzer): whereas the effects of heat transfer relate to temperature perturbations and therefore parcel density, the water vapour corrections are best described in terms of the 'crowding out' of dry air (and CO_2) molecules by water vapour molecules. In the context of an air parcel, the water vapour correction is not directly related to density. It may be worth noting that, were water vapour to have a molecular mass identical to dry air, the Webb corrections would still be necessary even though water vapour transfer would have no effect on parcel density.

Semantics aside, the Webb et al. (1980) corrections are correct, subject to the assumptions put forth by the original authors, while the Liu equations are mistaken.

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