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Interactive comment on “Calculations of automatic chamber flux measurements of methane and carbon dioxide using short time series of concentrations” by N. Pirk et al.

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I would like to introduce some clarity to the physics of the problems at hand.

First, as an aside, let us recognize that a gas analyzer combines the measurement principle of Beer’s law with its fixed laser volume to provide a direct measurement of the molar density. The wet molar fractions (in ppm) that the manufacturer provides in display or output necessarily require additional information regarding T and P in order to quantify the amount of air present. Unless the authors have used the identical values of T and P that the instrument software used to output wet molar fractions, they will have added error to the densities used in their model fits. It is generally important

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for scientists to know what their instruments are measuring, and not be deceived by instrument manufacturers with commercial interests.

Second, the "dilution" issue has not yet been appropriately addressed by the authors and this is readily shown by examining the ideal gas law in the form $n/V = P/(RT)$. For a fixed-volume chamber deployment that does not modify the state of the air, the total number of air molecules inside the chamber must remain constant. For simplicity and ease of illustration, let us consider a cubic chamber with 1-m sides, initially containing 40.9 moles of dry air only (0% water vapor) with composition according to the U.S. standard atmosphere (NOAA, 1976). Initially, therefore, the chamber would contain 31.9 moles of nitrogen, 8.6 moles of oxygen, 382 millimoles of Argon, and 13.5 millimoles of CO₂ (the remaining trace gases will be ignored here).

Now, let the chamber enclose during 100s upon a surface where the only gas exchange is an evaporation rate of 4 millimoles per square meter per second (corresponding to about 180 Watts per square meter), thereby adding 400 millimoles of water vapor. Because the chamber is not airtight, the addition of water vapor requires the exit of dry air components, in amounts according to 312 millimoles of nitrogen, 84 millimoles of oxygen, 3.7 millimoles of Argon, and most importantly 130 micromoles of carbon dioxide. Taking place over 100s, such a decrease in carbon dioxide within the chamber would be erroneously interpreted as 1.3 micromoles per square meter per second of carbon dioxide uptake, unless the appropriate correction (described by A. López-Ballesteros in terms of "dilution") were applied.

Please note that this correction is not proportional to the amount of water vapor in the chamber (initially 0%), but rather to the evaporation rate. Also, the magnitude of the flux correction does not depend on the size of the chamber, which was specified here only to simplify calculations. Thus, consistent with the original comment, unless the air is dessicated prior to being sampled, the correction of this problem requires tracking the water vapor accumulation inside the chamber, which is to say an indirect measurement of the evaporation rate.

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