

## ***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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We thank Ana López Ballesteros for her profound short comment on our manuscript. While we in principle agree completely with her remark about the water vapor dilution effect, we believe the corresponding errors are not higher than other errors connected to chamber flux measurements.

Gas concentrations can be given as densities, molar fractions or mixing ratios, making different distinctions about the presence of water vapor in the gas mixture. Our gas analyzers measure wet molar fractions (e.g. ppm as micromol CH<sub>4</sub> per mol wet air), which we convert to densities before applying the different model fits. This approach

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is explained in section 2.3 of the manuscript: “Note that gas concentrations are typically measured as a molar fraction (e.g. in units of ppm) and have to be converted to volumetric mass density (e.g.  $\text{mg m}^{-3}$ ) by means of the ideal gas (using T and P) law before Eq. (1) can be applied.”

Following Ana’s comment, we propose to clarify this approach by adding the sentence: “This approach neglects the presence of water vapor (which is not monitored in the chamber headspace) and the corresponding dilution effect on the measurements, which leads to an underestimation of the calculated fluxes which depends on flux magnitude, relative humidity and temperature in the chamber headspace, but is typically within 1-2%.”

The exact value of this underestimation can be assessed as follows: For example, at  $10^\circ\text{C}$ , 75% relative humidity and atmospheric pressure (which are typical conditions at our field sites during summer), the molar fraction of water vapor ( $W$ ) can be calculated from the vapor pressure of water (values found in e.g. Lide, 2005) as  $W = 1.2281\text{kPa}/101.3\text{kPa} \cdot 0.75 = 0.009$ .

The dilution effect on the gas flux ( $F$ ) can be estimated as  $F_{\text{wet}}/F_{\text{dry}} = c_{\text{wet}}/c_{\text{dry}} = 1 - W = 0.991$ , so our flux value is about 0.9% underestimated in this case.

Another effect of the water vapor dilution is that temperature and relative humidity might change (typically increase) during chamber closure. This is a more complex situation, and the error depends on exact temperature, humidity, chamber and instrument parameters, as well as flux values (e.g. Hooper et al., 2002). We did a rough simulation of relations between a “true”  $\text{CH}_4$  flux and its “measured” — according to our instruments and methods — value (see the supplementary information for this reply). Even if the temperature increased by  $2^\circ\text{C}$  (from  $10$  to  $12^\circ\text{C}$ ) during the 5 minutes closure time, and relative humidity increased from 75% to the maximal possible 100%, the cumulative error would still be within 1-2% of the flux value at the typical flux range of  $0.5$  to  $5 \text{ mg CH}_4 \text{ m}^{-2} \text{ h}^{-1}$ .

These effects of the absolute water vapor dilution, and its change during closure time, should mainly affect the flux estimate, but not the curvature of the concentration change. The curvature estimate would be affected only if the relative humidity and/or temperature changed in a time-dependent manner (e.g. increase first, then decrease again) during the closure time, so that such effects will be even smaller than the flux errors discussed above.

#### References:

Hooper, D. U., Cardon, Z. G., Chapin, F., Durant, M. (2002). Corrected calculations for soil and ecosystem measurements of CO<sub>2</sub> flux using the LI-COR 6200 portable photosynthesis system. *Oecologia*, 132(1), 1-11.

David R. Lide, ed. (2005). *CRC Handbook of Chemistry and Physics*. Boca Raton, Florida: CRC Press

Please also note the supplement to this comment:

<http://www.biogeosciences-discuss.net/12/C5638/2015/bgd-12-C5638-2015-supplement.pdf>

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