Possible artifacts of temperature and relative humidity changes on calculated fluxes from static chamber measurements.
Simulation exercise.

In this exercise we simulated positive CH_4 fluxes and studied the artifacts of their chamber measurements due to relative humidity and temperature changes.
Chamber parameters were similar to the ones described in the manuscript (0.6 m x 0.6 m x 0.3 m), exposition 5 minutes. Initial dry CH_4 molar fraction was set to 1.8 ppm, final dry CH_4 molar fraction ranged from 1.9 to 4.4 ppm (step 0.025 ppm, 93 simulations). The simulations imply linear increase in dry molar fraction from initial to final.
Applying different air temperature and relative humidity values for the initial and final moment, and implying their linear change during the measurement, we analyzed wet CH_4 molar fractions as those obtained from the gas analyzer, and calculated the fluxes according to our usual routine. The range of fluxes corresponded to Mastepanov et al., 2013 (0.2 to 6 mg CH_4 m^{-2} h^{-1}). In the end those "measured" fluxes were compared with "true" fluxes, error was expressed as deviation in % from true flux.

Case 1. Air temperature 10°C, relative humidity changed from 75% to 100%.
In this situation two sources of error are combined:

- static dilution effect: measured wet molar fractions are always lower than corresponding dry molar fractions, so all fluxes are underestimated;
- dynamic dilution effect: dilution is increasing during the measurements, which appears as a small negative flux at a stable dry CH_4 molar fraction. This error is high in % expression at low fluxes but becomes less and less important when fluxes increase.
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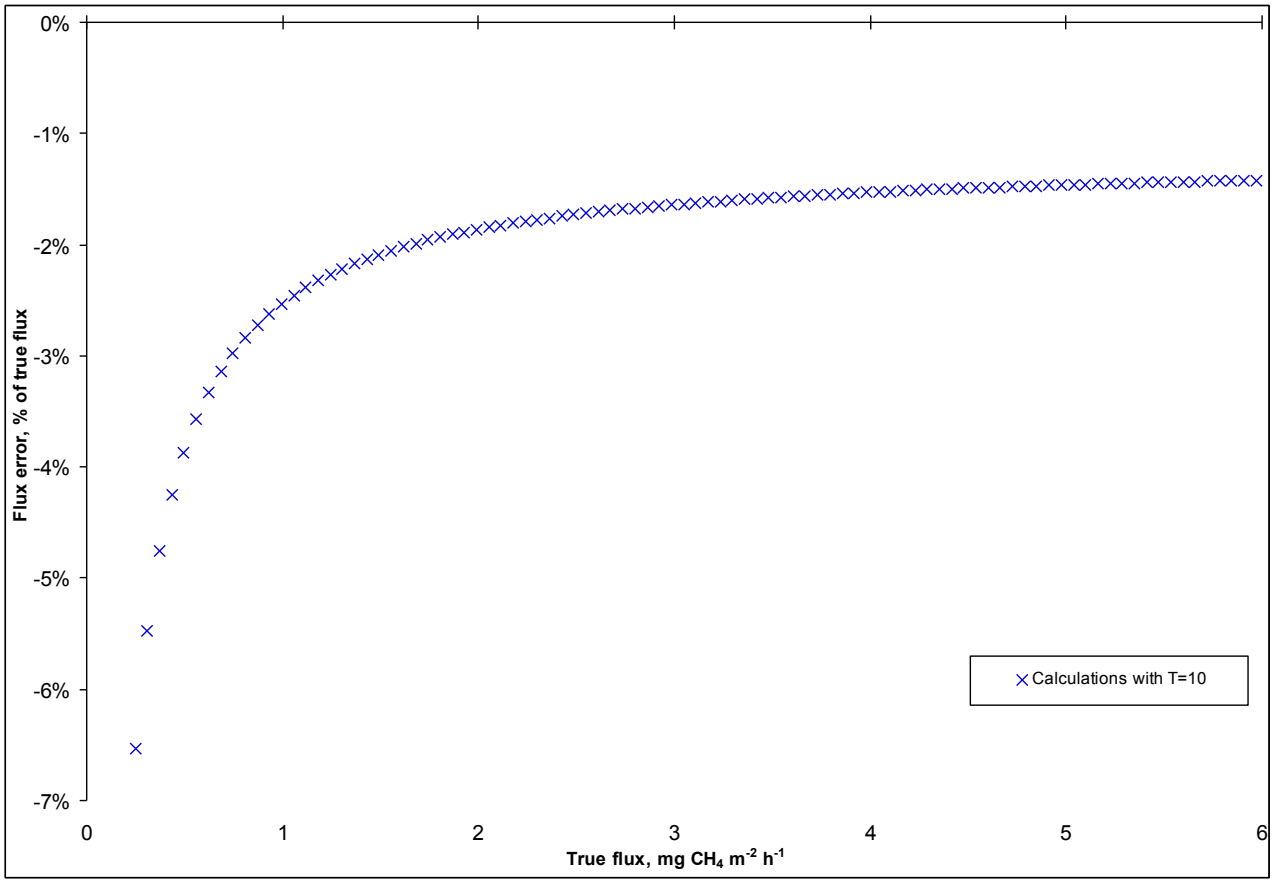
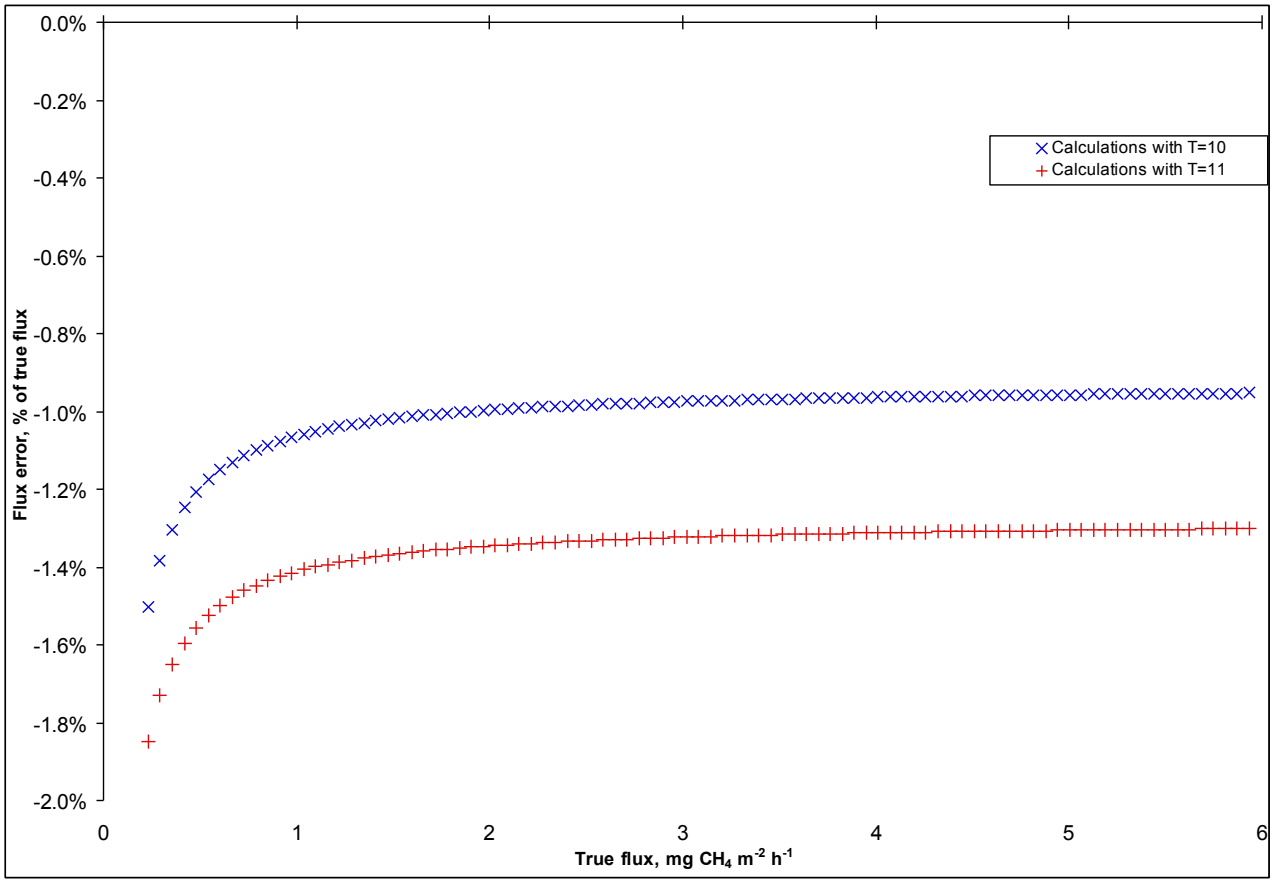


In this simulation the error in fluxes is estimated to be <2% for fluxes >2 mg CH_4 m^{-2} h^{-1} and relatively increased for lower fluxes.

Case 2. Air temperature changed from 10°C to 11°C, relative humidity changed from 75% to 100%.
This situation is more complicated:

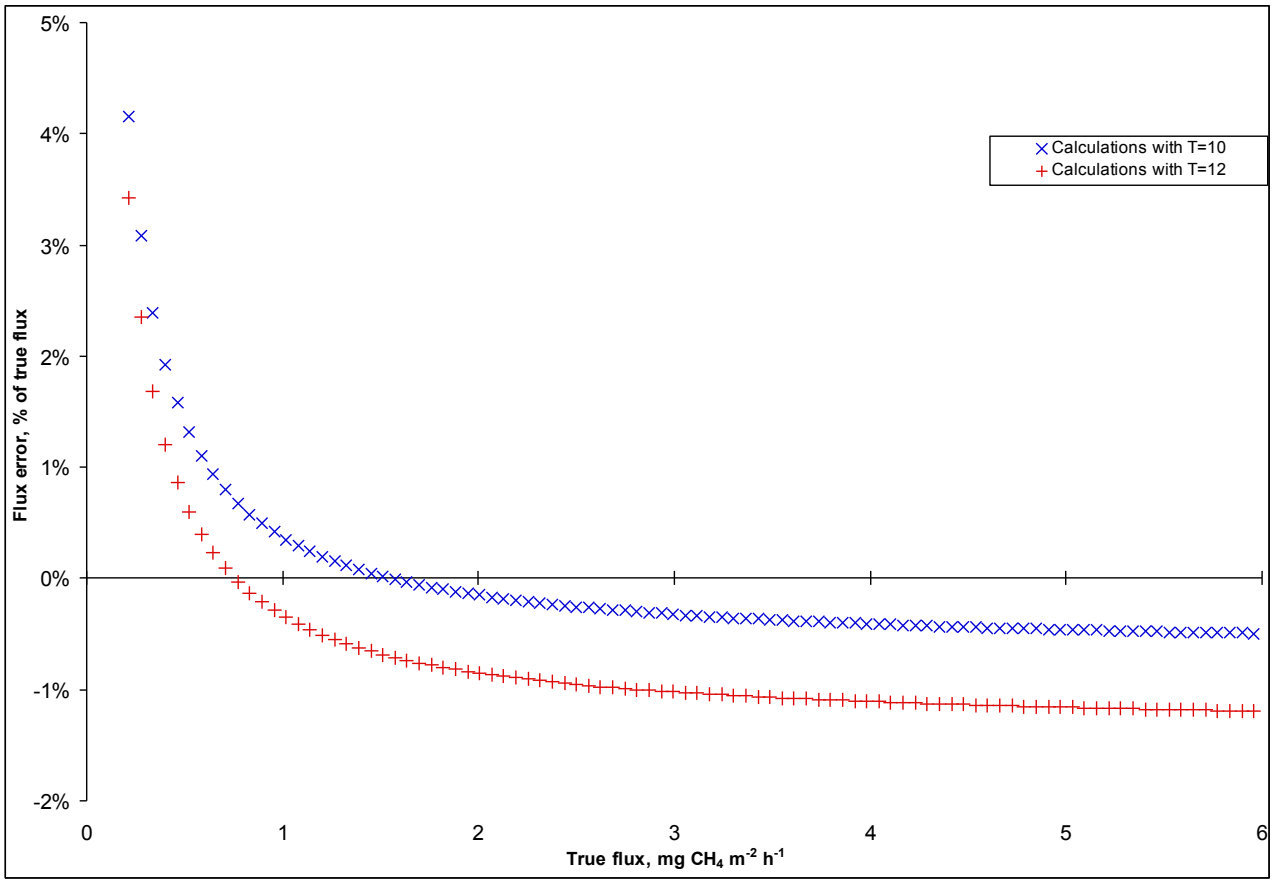
- static dilution effect is the same;
- dynamic dilution effect is enhanced, as the same relative humidity gives higher water content at higher temperature;
- temperature increase causes gas expansion, which is not accounted in our flux calculation routine.



Depending on what temperature value was used in the flux calculations, the cumulative error can be different. The error caused by not considering gas expansion to a large extend compensates the error caused by not considering the dilution by water vapor.

Case 3. Air temperature changed from 10°C to 12°C, relative humidity changed from 75% to 100%.

All the same factors, but both dynamic dilution and gas expansion are stronger.



In this simulation the effect of gas expansion is overriding the effect of dilution for low fluxes.

In reality, there are many other measurement errors, especially at low flux magnitudes, that make a high precision of flux estimation practically unreachable. Our simulation shows that changes in air temperature and humidity are not outstanding among them.

References:

Mastepanov, M., Sigsgaard, C., Tagesson, H. T., Ström, L., Tamstorf, M. P., Lund, M., & Christensen, T. R. (2013). Revisiting factors controlling methane emissions from high-Arctic tundra. Biogeosciences, 10(7), 5139-5158.