Anonymous Referee #2

Received and published: 7 December 2017

Review of the manuscript: "Calibration and Field Testing of Cavity Ring-Down Laser Spectrometers Measuring CH_4, CO_2, and δ13CH4 Deployed on Towers in the Marcel- lus Shale Region", submitted to Atmos. Meas. Tech. , by Natasha Miles et al.

The paper is describing the measurements of atmospheric mole fractions of δ13CH4, CH_4 and CO_2 at four sites in Pennsylvania. More precisely the manuscript describes the optimization of the technical setup based on lab and field tests.

The manuscript needs to be reorganized to reduce the back and forth between test descriptions and their results, which makes the reading quite difficult. There are too many redundancies, and unclear statement. When doing that I also suggest to shorten the manuscript. Some conclusions appear obvious, like for example the statement that field calibrations significantly improved the measurements compatibility. Also the so-called optimal calibration strategy refers to the design which was decided a priori and slightly modified during the campaign, but there was no plan to really evaluate alternative design. The conclusion should be written in a more concise way, focusing on the recommendations gained from the experiment.

Thank you for your thoughtful comments. We have addressed these concerns by reorganizing the bulk of the paper. Instead of strictly separating methods and results, we have now inter-mixed these, with the paper being organized by topic. I believe this does enhance readability of the paper. We shortened the paper by removing most of the discussion of choosing the optimal calibration study. As the other reviewer indicated, the isotopic ratio of the low tank (-23.9 per mil) would be better chosen to be closer to the measured values. We also eliminated switching from the target tank being independent to the low tank being independent in the text. Instead we just described how we actually processed the data, rather than describing all the options we explored. We have reworked the conclusions, focusing on the recommendations gained from our experiment and the potential of high-temporal-resolution isotopic methane data to constrain regional methane budgets.

Introduction: the introduction need to be reorder in order. For example the first paragraph of page 4 describing the interest of tower versus aircraft, appears between two paragraphs discussing more technical points about CRDS measurements

We reordered the introduction and added context concerning the utility of high-temporal-resolution isotopic methane data.

Page 4 / Line 13: “three field calibration tanks. . .”: I would rather say two calibration tanks plus one target tank used as quality control and not used in the calibration.

We changed this throughout the text to refer to these tanks as field tanks, since as you mention, one of them is independent of the calibration.

Allan variances tests; calibrations tests (Page 6 / Line 31): there are many back and forth between description of the set up and the results, which confuse the paper.

We have reorganized the paper to eliminate this concern. Instead of strictly separating methods and results, we have now inter-mixed these, with the paper being organized by topic. We believe this does enhance readability of the paper. While not the traditional method of manuscript organization, it is sometimes used (e.g., Rella et al. 2015).

Page 9: In-situ field calibration: is the Nafion required for the setup ? Have you compared possible biases due to the use of the Nafion versus the water vapor correction ? I am not fully convinced by the strategy of humidifying the dry calibration tanks.

Rella et al. (2015) noted that the effect of water vapor on the isotopic ratio of methane is large (up to 1 ‰) and nonlinear. Thus no water vapor correction is available. They recommend drying to less than 0.1% mole fraction. We have added clarification on our reasoning for drying to the text. We also added a reference to Andrews et al. (2014) who document the technique of drying the sample and humidifying the calibration gases.

Page 9: 4 min flushing: how do you estimate those 4 minutes as sufficient for the flushing ?

Added to the text: After this time, the CO_2 and CH_4 mole fractions have stabilized.

Page 12: background site: why don't you select the background site as a function of wind direction rather than picking up one site for the full period ?

We added to this discussion. It now reads, ". The predominant wind direction for the Marcellus region is from the west (Fig. 4). For westerly winds, the South tower is a reasonable choice for a background tower. The South tower measured the lowest overall mean afternoon methane mole fraction (1960.2 ppb CH_4). The mean afternoon methane mole fractions of the other towers, averaged only when data for the South tower exist, were 8.7, 7.0, and 2.9 ppb higher, at the North, Central, and East towers, respectively. For future analyzes, a wind direction dependent background tower (South or North) could be used, but the North tower did have the largest mean enhancement in CH_4 mole fraction compared to the South tower. "

Page 14: Allan results: For CH_4 and CO_2 it should be noted that the results seem to be not as good as the performances obtained with G1301/G2401 analyzers. Do you know the reason which could explain a difference of the performances between those analyzers ?

We have added further clarification to the Allan deviation results section and the side-by-side testing section. The performance of the G2132-i analyzers in terms of CO_2 precision is worse than that of the G2301/G2401 analyzers primarily because a weaker spectral line is used. Whereas the spectral line for CH_4 is the same between the two types of analyzers, for CO_2, the absorbance of the spectral line used in the G2132-i analyzers is a factor of 11 times less, meaning the precision is dramatically reduced.

Page 16: Calibration scheme: the presentation of the different tests should probably be shortened. Is there a difference between Expt E and H designs ?

We have eliminated most of the EXPTs in order to simplify. We eliminated Table 3 and shortened Table 4 from the original document. EXPTs E and H are no longer described.

I would appreciate an evaluation of the optimum frequency of the field calibration sequences (intermediate between 0 and once per day). From the variabilities shown on Fig.8 and 9 it looks like a reduction of the calibration frequency to once every few days would not affect by much the measurements.

We added to the text, 'Considering shorter term changes, the day to day changes in the calibration were less than 0.5 ‰ for December 2016. Less frequent calibrations, e.g., twice per week, could be considered, but the reduction in field tank use is not large considering the low flow rates of the instruments and steady changes up to 2 ‰ in the raw data over the time scale of days were observed in Rella et al. (2015). '

Fig.8: the legend is misleading since the so-called target tank is used as a calibration tank. To make it clear you should add comments in the legend of each figure (e.g. Target tank (used as CAL))

We added to the caption, "The target tank was used in the isotopic ratio calibration, whereas the low tank was independent."

Page 17: Fig. 9B and 9C should rather be 9A and 9B

Corrected.

Page 20 Line 27: suppress 'For the daily afternoon averages,'. Not clear what you mean by a 'reduction' of 0.6-0.7pmil.

We have clarified these confusing statements. The text now reads, "The standard deviation of the daily afternoon averages (rather than 10-min averages) was 0.6 – 0.7 ‰. Thus the observed width of the distribution appears to be persistent throughout the afternoon and not merely measurement noise. "

Page 20 Line 32: Why do you compare CH_4 enhancements (6ppb) with $^{13}CH_4$ target compatibility (0.2pmil) ?

Typo corrected.

Page 21: lines 22/23: Unclear statement about the dilution of local source.

We have removed this statement.

Page 21: lines 22/23: The discussion about the source signature need to be clarified, or preferably merged in the discussion section.

Hopefully having the paper organized by topic, rather than having the method for each topic separated from the results, makes this discussion more clear. We also added a figure of an example time series of a peak for which we applied this method.

Page 23: lines21/22: unclear statement.

A misplaced parenthesis made this statement confusing. Corrected.

Conclusion: in your last sentence I would like to see also a comment or discussion that the strategy of using continuous measurements at four tower is maybe not the optimal one for the quantification of such sources.

We added, ' For determination of the source signature for a specific known location, the tower-based approach is not ideal. Instead the strength of the tower-based approach lies in covering larger areas and many potential source locations, and for longer periods of time than is feasible by other approaches, e.g., short-term mobile techniques. ' We also added to the last section discussion about the utility of high-temporal-resolution methane isotopic ratio data for constraining regional methane budgets.

Please also note the supplement to this comment: https://www.atmos-meas-tech-discuss.net/amt-2017-364/amt-2017-364-RC2-supplement.pdf

Interactive comment on Atmos. Meas. Tech. Discuss., doi:10.5194/amt-2017-364, 2017.