General Comments

This manuscript discusses a specific question within the scope of AMT, presenting new data on the difficult task of calibrating laser methane isotope instruments at unmanned tower sites.

The methods are outlined in extensive detail, but this also highlights how a little more consideration of the isotopic signatures of influencing methane sources at the start of the project could have saved significant time spent later refining calibration routines. The choice of enriched calibration mixtures over deleted ones suggests an expectation of 13C-enriched sources.

Thank you for your thoughtful comments. We shortened the paper by removing most of the discussion of choosing the optimal calibration study. Instead we described how we actually processed the data, rather than describing all the options we explored. We agree that the choices of field tanks and the field tank testing times were not ideal and have added specific recommendations for future similar networks to the paper.

In places the manuscript is quite difficult to follow as there are frequent references to previous or subsequent sections. There are also a lot of small errors that need tidying up, and some points that need greater clarification. This includes the selection procedure of points for the individual peak Keeling plots. Some of the subsequently ’unused’ EXPTs could be removed from the text (but remain in the table), as they are not used in the revised calibration routine.

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. 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). We also added an example of a time series used for the individual peak Keeling plots, as suggested. We removed lengthy discussion of calibration procedures not actually used to process the data.

The manuscript also lack a good final summary, possibly due to the conference volume time constraints, but it would be good to see the following questions discussed at the end: 1) In hindsight what could have been done differently? 2) What are the recommendations for anyone else undertaking the set-up of a similar network? 3) What are the limitations and advantages of the CRDS technique at fixed tower sites compared with IRMS at a similar type of site (e.g. Rockmann et al., 2016)?

We have reworked the final section to include recommendations for future similar deployments and have mentioned the potential of high-temporal-resolution methane isotopic ratio data, when combined with modeling, to constrain regional methane budgets. Previously the utility of networks of such data was not mentioned.

The manuscript also highlights the need for suitable isotopic standards for urban / source region standards within this community, as the measured isotopic ratios fall between those commonly measured at source, or the tight constraints around -47 ‰ needed for background sites. Something like -52 and -42 ‰ at 3 ppm mole fraction are toward the limits of the enhancements measured at such sites, and so would be very useful as standards.

We included recommendations for future work with these thoughts in mind.

Detailed Comments

Abstract (see also later comments)

Page 1 Line 24 – Why only calibration with high methane mole fraction air bottles?

We edited that sentence to read, “Prior to deployment, each analyzer was tested using bottles with various isotopic ratios, from biogenic to thermogenic source values, which were diluted to varying degrees in zero air, and an initial calibration was performed.” We were referring to the Isometric Instruments bottles (as high methane mole fraction air bottles). We did only use the high mole fraction mixture in the initial calibration prior to deployment, because the field calibrations supersede the correction of the mole fraction dependence of the isotopic ratio (and because we didn’t measure the low mole fraction mixtures long enough). Those details are in the text, but are too detailed to describe in the abstract. Thank you for pointing out the confusing statement in the abstract.

Page 2 Line 2-5 - This technique might work here because the Marcellus gases are significantly enriched in 13C, but in many regions (eg. Australia, much of the EC) there are no major sources enriched in 13C relative to atmospheric background, so that the sources would be very difficult to distinguish far away from the point of emission.

Good point. We added a sentence to the conclusions, "We note that the Keeling plot approach to determine source isotopic signatures far from the point of emission will be difficult to apply in regions without sources that are significantly depleted or enriched in 13CH4 compared to ambient."

Page 2 Line 4 – What is the error on the -31.2 ‰ The literature suggests a range of source values.

We added the standard deviation of values that we determined and edited the last phrase to read, " within the wide range of values consistent with a deep-layer Marcellus natural gas source. "

Main Text

Page 3 Line 18 – t missing from Schweizke

Corrected.

Page 5 Lines 16-22 – yes it should be symmetrical at 35 and -60 ‰ around a back- ground of -47.5 ‰ but the colours on Fig 1 don't show an even change to enriched and depleted values around the background composition (see also comment on Figure).

Yes, thank you for pointing out this error. We have corrected the calculations for the figure to reflect -35 and -60‰, with a background of -47.5‰ used. We added further description of the end members to the caption, as requested.

Page 6 Line 3 – the noise is known to be less for higher mole fractions – please cite the source of this

We added the reference for this (Rella et al., 2015).

Page 6 Line 24 – slight clarification needed – was 1 sccm for the standard line and 500 sccm for the zero air line

Yes, and we have added that clarification.

Page 7 Lines 1-7 – it would be useful here to include the flow rate through the instru- ment to give some idea of how much cal gas was being used.

We noted in this section: "With the flow rate of 0.400 sccm for the isotopic standard bottles, the total volume of standard gas used was 88 cc." Here we focused on the standard bottles rather than the zero air, since the zero air is inexpensive. We also added in Section 4.3 (In-situ field calibration gas system), "The flow rate of the instruments was 35 cc/min, and the 150A tank size was used, corresponding to 4.021 x 10^6 cc at standard pressure and temperature. Thus there was gas sufficient for 9800 calibration cycles, or 725 days at this calibration frequency."

Page 7 Lines 19-32 – some of the terms are not clearly explained here (for example Bdefault) so please either clarify or remove and refer the reader directly to Rella et al. (2015).

We added a description of the meaning of the terms B and Befault.

As it would be good to be able to refer to the calibration plot at this point to see the isotopic offset compared to known values for each standard at different mole fractions can Fig.7 go here, or be linked to section 4.2 or at least referred to?

With our reorganization of the paper, the figure is included in the mentioned section.

Page 8 Lines 3-10 – The study area section and accompanying figures seem a little out of place here as the sites are not discussed for a long time. Is there a better position for this?

We moved the section describing the study area (including the figures originally numbered 3 and 4) to just prior to the section describing "Methods for determining enhancements".

Page 8 Line 16 – not been demonstrated for laser instruments, for IRMS see Rockmann et al.(2016).

We added "CRDS" to the sentence.

Page 8 Line 25 – using the word 'sampling' for the measurement of standard cylinders is easy to confuse with the actual measurement of ambient air at the towers. Is there an alternative word that could be used for this procedure?

We changed this to 'testing' throughout the text.

Page 8 Lines 26-27 – the reasoning behind choosing the mole fractions for tanks with these isotopic standards is not clear here, and is even less clear later when the -24 ‰ cylinder is dropped from the calibration routine.

Agreed. In retrospect that is clear. We added, "We note that it would have been preferable to utilize calibration tanks closer to the observed air samples in terms of isotopic ratio. In particular, the high tank could have been spiked with the –38.3 ‰ bottle, and/or both the high and the low tanks could have been spiked with a mixture of the –38.3 and –54.5 ‰ bottles. "

Page 9 Lines 11-13 – what is a large flow rate and what is the delay time for air entering the inlet to instrument measurement?

We added, "For the CRDS analyzer, air was drawn down the tube at 1 L/min, with 30 cc/min flow into the analyzer and the remainder purged. The residence time in the tube was about 1 min. Separate tubes were used for the CRDS and flask sampling lines because of the differing flow rates (varying between 0.29 and 3.8 liters per minute) required for the flask samples (Turnbull et. al., 2012) and to ensure independence of the CRDS and flask measurements. "

Page 9 Lines 28-30 – should the aim not be to achieve the best possible precision, not just to reach target compatibility? Would the high mole fraction tanks not achieve better precision if analysed for 32 minutes? If the shorter times are chosen just to save cal gas then it should be made clear somewhere.

We added to that paragraph, "The ideal calibration tank testing time is a balance between minimizing calibration gas usage (and consequently maximizing ambient air sampling time) and achieving sufficient precision. "

Page 10 Lines 18-24 – the -24 ‰ standard at any concentration was never going to be useful at the tower sites as it is even beyond the range of sampling a pure source emission. A clear understanding of the maximum mole fractions and isotopic shifts observed at the towers would have been useful before production of the working standards for these sites, even if it meant not using the first 6 months of isotope data.

Page 13 Lines 26-27 – what are the uncertainties on the NOAA tanks?

Uncertainties have been added to the text.

Page 14 Lines 8-10 – replace tubing with tube, and on-board with internal

Done.

Page 14 Section 5.3 – what is the relevance of this section? Unless the results of this test are shown somewhere, and referred to here, then is this section necessary for the points under discussion?

We added clarification that although not central to the primary results of this project, the performance of the analyzers is important if the data are to be used as part of the continental-scale CO2 network. The results are shown in Section 6.6.

Page 14 Line 16 – 14:00-15:00 isn't late afternoon

Replaced with "afternoon."

Page 14 Line 18 – do you mean measured? Either 'samples were collected' or 'flasks were filled'

Replaced with "samples were collected."

Page 15 Lines 9-10 – 'An error in isotopic ratio as a function of isotopic ratio' is not very informative. Figure 7 shows that there is an offset in the measured isotopic ratio as a function of the changing known isotopic ratio, which seems to be quite constant for all instruments at higher mole fractions, but instrument-specific at near-background mole fractions.

We added this clarification to the text.

Section 6.2 – I initially thought that the experiments involved changing over to different cylinders, which seems to be the case when changing to the new calibration routine, but most of these EXPTs seem to be just manipulation of the data for different standards, so please can you make clear at the start of this section that these are mostly changes in the calibration calculations and not changes to the cylinders being analysed. Some of the results of these experiments are not used as they do not improve the required precisions. Do these need to be described in the text?

This section was confusing and we have eliminated all but two schemes (using the target as independent and using the low as independent). We eliminated Table 3 from the original document. And we tried to clearly state when hindsight (and insightful reviewer comments) have revealed things that we would do differently.

Page 16 Line 13 – a result is a result and cannot be changed. Do you mean 'improve the calculated precision'?

Changed to "improve the calculated accuracy." Also replaced in three other locations in the text.

Page 18 Line 16 – 0.18 ‰ is stated above this as the daily average, not the hourly average as used here.

We clarified that section to indicate more clearly that averaging over the low tank for each day totaled about 1 hour of data (actually 81 min), and thus the standard deviation of these values is a proxy for the noise due to the calibration scheme in the hourly sample air data.

Section 6.6 – the side-by-side testing results are mentioned here, but have a lot of content overlap with the methodology for side-by-side testing. Does this have to be in two places? It isn't particularly relevant to the core isotopic story.

We were careful to keep the methods and results separate. We added clarification in Section 5.3 that although not central to the primary results of this project, the performance of the analyzers is important if the data are to be used as part of the continental-scale CO2 network.

Page 20 Line 2 – 'mean flask' – is this referring to the rapidly-filled or the hour-long filled flasks?

This was specified in the prior section as being the hour-long filled flasks.

Page 20 Line 5 – 'hourly flask to in-situ differences for the year'. It isn't clear what this means

This was repetitive with the prior section and makes it sound more complicated that it is. We removed it.

Page 20 Line 19 – 'The time scale of the individual data points was 10 min'. Do you mean averaging interval?

Yes, corrected.

Page 20 Lines 32-33 – It isn't clear why 'enhancements greater than 6ppb CH4 in magnitude' are '3 times the target compatibility of 0.2 ‰

Typo corrected.

Page 21 Line 15 – mean of -31.2± ? ‰

-31.2 ± 1.9 ‰. Added to text.

Page 21 Lines 21-23 – this section needs sorting out; firstly they are not peak heights but enhancements over background, and it is a 2.5 to 8.7 ‰ positive shift in measured isotopic ratio. What does ‘ reduced methane enhancement at other data points within the peak’ mean? If the maximum enhancement is 2008 ppb, why does it mention 1500 ppb maximum earlier?

We made these changes and removed the confusing phrase as it is too obvious. The maximum enhancement during non-afternoon hours at the central tower was 2008 ppb. The 1500 ppb mentioned refers to afternoon hours at the North tower. We added clarifications.

Page 22 Line 21 – remove the s from fractions

Done.

Page 22 Line 26 – replace improving with improved

Done.

Page 22 Lines 35 to 37 – given the availability of the Isometric flasks, my preference for a calibration would be to create a high and low mole fraction cylinder from both of the - 54 and -38 ‰ standards, used in combination with a low ambient cylinder and a similar target gas, or at least a high and low at -38 ‰ as that is the direction your sources are taking the ambient mix. More cylinders, but it should improve the correction in the triangle of 13C-mole fraction space where the measurements lie.

We have incorporated these ideas into Table 4 of the revised manuscript, for recommendations for future tower networks of CRDS isotopic methane analyzers.

Page 23 Line 30 – an isotopic ratio enhancement of -0.6 ‰ Two problems with this: surely this should be a + and not a -, and how do you enhance a ratio? Normally this would be heavy or light for a change in ratio as 13C increases or decreases, or enrichment or depletion if talking about the individual 13C, so it does represent an enrichment in 13C.

It seems that “difference from background isotopic ratio” is a better term than “enhancement above background” – I can see how the latter is confusing. I switched the terminology throughout the text. If the source in question is -35 ‰ and background is -47 ‰ (as in the example in the text), the measured isotopic ratio would be lower than background, so I think it is negative. I’m assuming it was just the term “enhancement” that was causing the problem.

Page 24 Line 15 – already presented so should be ‘ we have presented.

Done.

Page 24 Lines 15-19 – this is a rather abrupt ending – see general comments for suggestions of what to add in summation.

References
All those present seem to be correct in the text, just move the date on P27 Line 7 up a line.

Done.

The following references are mentioned in the text but are not in the list: Conway et al., 2011 Montzka et al., 2011 Turnbull et al., 2012 Vaughn et al., 2004

These have been added to the references list.

Tables

Table 2 – Not clear what this table is representing from the caption? Are these due to interferences with the 12CH4 and 13CH4 spectral lines? What is the maximum CH4 at these sites and does this increase or decrease the interference on each of these species?

We clarified the caption of Table 2, "Maximum error estimate attributable to cross-interference due to direct absorption on $\boldsymbol{\delta}$13CH4. These estimates were based on typical values for this tower-based application and estimated effects on CRDS measurements (Rella et al., 2015), and assumed 2 ppm ambient CH4 mole fraction. For water vapor and carbon dioxide, the interferences are independent of CH4 mole fraction for 1 – 15 ppm. For the other species listed, the interferences are inversely proportional to CH4 mole fraction. "

Table 3 caption Line 10 – should be at not and

Done.

Table 5 – the alternative strategy looks to be the best, but given the observed range of measurements up to 4 ppm, would it not be better to correct with a lower precision at 4 ppm than a calculation of the offset from 10 ppm?

This is a good question. The choice of the CH4 mole fraction of the high tank is based on the optimal determination of the calibration coefficients c0 and χ, rather than the expected range of ambient CH4 mole fractions. The effect of the offset parameter c0 on the calibrated δ is largest at low mole fractions, whereas the effect of the slope parameter χ is independent of mole fraction. Thus the ratio of the high and low tank mole fractions determines how separable the two effects are. We therefore chose the high tank mole fraction to be as high as possible without introducing other nonlinearities into the system. We have added this explanation to the text.

Table 5 - You have all of the Isometric standards available, so 'easier to obtain tanks with these ratios' is not an advantage of the reduced compatibility option, but all of the options.

We have reworked Table 5 (now Table 4) to make it more clear.

Figures

Is there a way to sort out the superscript and subscripts on the vertical axes of the graphs or is this a software limitation?

The superscripts and subscripts have been fixed.

Figure 1 - It needs to be mentioned in the caption what are the signatures of the isotopic end members used to create this plot. There is an uneven spread of colour change around the -47 ‰ point, which suggests that this has been calculated with -30 and -60 ‰ source increments and not the -35 and -60 ‰ mentioned in the text.

Yes, thank you for pointing out this error. We have corrected the calculations for the figure to reflect -35 and -60‰, with a background of -47.5‰ used. We added further description of the end members to the caption, as requested.

Figure 2 caption – mention the cylinder volumes

Added: "At standard pressure and temperature, the gas volume of the zero air and working standard tanks was 4021 L and that of the Isometric Instruments bottles was 28 L."

Figure 4 – The lowest category of wind direction is 0-2 m/s, but the caption states that calm winds below 3.6 m/s are not categories by direction, so two things to correct here. 3.6 m/s is not calm. I think that this is a scale conversion problem from km/h, and calm should be either less than 1 m/s (in which case the lower category displayed should be 1-2 m/s), or <0.1 m/s.

3.6 m/s was a typo. Further clarification to the caption has been added. "These afternoon means were based on hourly reported measurements. For the hourly measurements, calm winds (< 1.6 m s^{-1}) were not categorized by direction and thus were not included in the afternoon mean. For the hourly measurements, calm winds (< 1.6 m s^{-1}) were reported as zero and were included in the afternoon mean. "

It isn't clear why Figs 3 and 4 are so early in the manuscript. Until the tower location data is discussed there isn't really the interest in seeing these influences.

We moved the section describing the study area (including the figures originally numbered 3 and 4) to just prior to the section describing "Methods for determining enhancements".

Figure 5 – What is the flow rate of the pump on the exhaust line (ME3)? It looks like it should be balancing out the ambient inlet flow.

Yes, the flow rate is about 1 LPM. We added that information to the figure, and also changed the labels of the tanks to be consistent with the text.

Figure 6 caption – incorrect 13C shown on first line

Corrected.

Figure 7 – The residual errors seem to be quite consistent between instruments for the higher mole fraction cylinders at all sites. The correction procedure for the small number of elevated mole fraction samples is not very obvious from the text.

The calibration procedure is described in Section 3.2.2.

Figures 8 and 9 – what are the error bars for these data points? If they cannot be added to the graphs can they be alluded to in the caption?

We added to the caption of Figure 8, "The Allan deviation for time period used for each calibration cycle was, for the period prior to the improved tank sampling strategy, 0.2 ‰ for the high tank, and 0.5 ‰ for the low and target tanks. Following the implementation of the improved tank sampling strategy, the Allan deviation for each calibration cycle was 0.1 ‰ for the high tank, and 0.3 ‰ for the low and target tanks. ", but it is not obvious how to calculate an estimation of the error for Figure 9.

Figure 11 – Can North, Central and East be labeled at the top of each column?

Done for this figure, and for Fig. 7.

Figure 13 – add measured before isotopic in the first line of the caption. The big delta small delta use on the left column horizontal axes is not explained. The x104 used in the right column needs correctly positioning, although it would be much clearer just using 0.2 to 0.6 in 1/CH4 ppm.

Done for this figure, and Figs. 14 and 15.

Figure 14 – the 15 ‰ spread of isotopic ratios measured at near background mole fractions reduces confidence in the data. The text suggests that there is a gradual improvement in measurement precision as the mole fraction increases. The Keeling plots suggest that the transition is quite sharp, and the isotope CRDS that I have seen in field operation seem to have a sharp improvement at 7-8 ppm CH4, so can this be clarified in the caption or elsewhere in the text.

Yes the range of values during non-afternoon hours at the North tower is 15 ‰, but the standard deviation is much less, only 0.76 ‰. The size of the markers in the figures makes it look more variable than it is. I reduced the marker size, which helped a little, but I don't think we can eliminate this without making the figures very large. Thus I added the median and standard deviation of the isotopic ratios at each tower to the Figs. 13/14 CFI, (Fig 14/15 in the updated document) in order to clarify the variability. The noise in the isotopic ratio measurement does increase near background mole fractions, but it's about 0.4 ‰ for 10 min averages at 2 ppm CH4. We added this to the captions for Figs. 13 and 14 and in the text. We added a figure showing the exponential decease of the standard deviation of the methane isotopic ratio at 2, 3, 6, and 7 ppm.

Figure 15 – the Keeling plots are good but indicate very little variation in measured isotopic ratio for a given mole fraction even at near background mole fractions. Are all of the points from these peaks used? It would be good to see the actual time graph of the isotopes for 1 of these graphs to see the points that have been selected for use in the Keeling plot. The source intercept calculation is without errors. Can these be calculated?

We added a figure to the Methods Section indicating an example of the CH_4 time series for which the Keeling plot approach was applied. The time during which the tower was in the plume of the source was obvious, and only these points were included in the calculation, thus explaining the lack of variability. Added to the text, "Propagating a potential error (attributable of analyzer uncertainty) of 0.2 ‰ at the heavy end of the Keeling plots and –0.2 ‰ at the light end, and vice versa, the potential range of the mean is from –32.0 to –30.4 ‰. "

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