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Atmospheric Measurement Techniques
Discussions

Interactive comment on “Calibration and Field Testing of Cavity Ring-Down Laser Spectrometers Measuring CH$_4$, CO$_2$, and δ^{13}CH$_4$ Deployed on Towers in the Marcellus Shale Region” *by* Natasha L. Miles et al.

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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.

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.

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)?

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.

Detailed Comments

Abstract (see also later comments)

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

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.

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

Main Text

Page 3 Line 18 – t missing from Schweizke

Page 5 Lines 16-22 – yes it should be symmetrical at 35 and -60 ‰ around a background 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).

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

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

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

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). 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?

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?

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

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?

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.

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?

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.

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?

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

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?

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

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

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.

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?

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

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

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.

Page 20 Line 2 – ‘mean flask’ – is this referring to the rapidly-filled or 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

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

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 ‰ ÌĄ.

Page 21 Line 15 – mean of -31.2± ? ‰

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?

Page 22 Line 21 – remove the s from fractions

Page 22 Line 26 – replace improving with improved

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.

Page 23 Line 30 – an isotopic ratio enhancement of -0.6 ‰Ṫwo 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.

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

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.

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

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?

Table 3 caption Line 10 – should be at not and

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? 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.

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?

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.

Figure 2 caption – mention the cylinder volumes

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. 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.

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.

Figure 6 caption – incorrect 13C shown on first line

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.

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?

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

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.

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.

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

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