

Interactive comment on “Characterisation of $\delta^{13}\text{C}$ source signatures from methane sources in Germany using mobile measurements” by Antje Hoheisel et al.

Anonymous Referee #3

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General Comments

This paper presents a measurement setup used to determine the isotopic signatures of methane sources in Germany. The measurements are done with a CRDS instrument allowing direct measurements of samples or mobile measurements close to the sources. The authors have used the AirCore method to precisely determine the CH_4 isotopic signatures while crossing plumes of targeted sources.

The paper is well organized, and a particular attention has been addressed to present and correct the well-known cross-sensitivities introduced by the CRDS. The instrument is also well described and characterized, but the calibration strategy and the data qual-

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ity insurance remain unclear to me. In addition, the part describing the mobile measurements and the AirCore technique lacks of details for a measurement technique paper (see my questions/comments in the specific comments).

The results are clearly described and compared with other studies. It is then much of interest for the scientific community as it participates to the general effort for increasing the scientific database of CH₄ isotopic signatures. It is nevertheless regrettable that the C₂C₆ to CH₄ ratios are not presented along with the isotopic signatures. I strongly suggest to add it in order to give the paper more visibility.

Specific comments

The language used in the manuscript is not always precise. For instance, the terms “¹³C values” and “¹³C signatures” are not the same and sometimes confusing as used in the MS. Also, the ¹³C signatures are not directly measured by the CRDS but determined after data treatment from the measurements. Please correct through the all manuscript.

Most of the time, the uncertainties are presented, but without any explanation on how they are calculated and which parameters are used to computed them. It is also not clear what is the difference between uncertainties and precision. For instance, page 9 line 5/6, it is stated that increasing the number of data point improves the uncertainties on signatures. The next sentence, “uncertainties” has been replaced by “precision”. It is confusing. Please clarify through the all manuscript.

The G2201-i instrument can be used in different mode, which drives the measurement frequency of each species. Also, the methane is reported by the instrument in high range (HR) and high precision (HP) mode depending on the level of the measured mole fractions. This drives the instrumental precision. Please, add some details on these two points.

Part2.1.2 and figure 1: here is a list of questions/comments which should be addressed:

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- how are the valves switched? - how is the flow measured and/or controlled? -why the flow presented here differs so much from the laboratory setup (160ml/min vs 20 to 80ml/min)? - what is the typical air flow going through the AC in monitoring mode? - what is the typical vehicle speed while in monitoring mode? - in figure1, the blue and green arrows are difficult to differentiate. Please, make them thicker.

Part3: how do you make sure that the direct samples are not mixed with ambient air? This could bias the isotopic signatures.

Part 3.2: it has been shown in figure5 that the CH₄ peak height above the background is mostly driving the fit error. It would make much more sense to present all the peak heights above the background instead of the absolute CH₄ value.

Conclusion: the Miller-Tans and Keeling approaches give the same results. Why do you suggest using one instead of the other one?

P1, line 6 : C₂H₆ only affects the ¹³C measurements

P1, line 11: ¹³CH₄ signatures instead of values

P2, line 1: “biogas burning” is not a CH₄ source

P2, line 11: do you mean “due to its origin,”?

P2, line 15: introduce IRMS here and not line 17, and add what GC stands for.

P2, line 16: I suggest to delete “has been” → as shown by Röckmann et al.

P3, line 1: replace signature by ratio. Signatures are not directly measured by the CRDS.

P3, line 13: it is surprising to observe such a flow range (factor 4). Could you explain why and give more details? Is the flow controlled somehow?

P3, line 17: what do you mean by synthetic air? Have you checked it is CH₄ free?

P3, line 20: do you keep the 15min or is there a stabilization time?

P3, line 25: decabon

P3, line 33: 160ml/min to be consistent with the previous part.

P4, line 5: How the measurement precision can be better in replay mode than in monitoring mode with the same instrument? Please clarify?

P4, line 30: have you tested the Nafion for potential fractionation?

P5, line 29: Assan et al. 2017 showed that the intercept changes in time due to baseline drift. Have you regularly checked it?

P5, line 33: please, check the unit

P6, line 1: what do you mean by fully?

P6, line 6: you cannot get a concentration range with a single cylinder. Please reformulate.

P6, line 8: as I understood, a one point calibration strategy is used, meaning that you assume that the instrument has a linear response through the all measurement scale (mobile and sample measurements). Then why two different cylinders are used as calibration gases?

P6, line 10: have you seen some changes in the CRDS regime before and after each experiments? What was the maximal drift observed and how are they taking into account?

P6, line 4 to 11: it is not clear to me how the CH₄ is calibrated. There is no CH₄ calibration factor in Table1.

P6, line 25: Please, detail how these uncertainties are calculated.

P6, line 32: is it the last 10min over the 15min measurements?

P7, line 5: is it a linear drift? The uncertainties is larger than the drift itself.

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P7, line 19: please clarify which uncertainties you are talking about.

P7, line 23/24: were you driving while analyzing the AC? Micro-vibrations due to vehicle motion degrade the CRDS performances.

P7, line 25: do you mean uncertainties? Is that calculated only from the fits?

P8, line 17: isotopic signatures are not directly measured

P8, line 33: do you mean the fit error? Or is there more parameters used to derived the uncertainties?

P9, line 10: what precision?

P10, line 17/18 : these criteria are already described earlier, no need to state it again here.10

P10, line 20: why is the daily mean used and not the single signatures? Same p13 line 6.

P11, line 30: what is the peak height of the third AC? Please replaced value with signature.

P14, line 10; replace the dot with and.

P14, line 11: I suggest to replace monitor by sample.

P14, line 15: choose between “always” and “mostly”

P14, line 16: only peak heights are measured, not fluxes. I would then delete “therefore” and add “from these natural gas facilities”.

P15, line 3: what is the detection limit of the system? Are you sure there is plumes coming out?

P15, line 6: check for typo.

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