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Reply by the Authors to “Comment on acp-2021-76”

Anonymous Referee #1

Referee comment on "Isotopic Signatures of Major Methane Sources in the Coal Seam Gas Fields and Adjacent Agricultural Districts, Queensland, Australia" by Xinyi Lu et al., Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2021-76-RC1, 2021

My comments are attached as a supplement PDF file.

Please also note the supplement to this comment:
https://acp.copernicus.org/preprints/acp-2021-76/acp-2021-76-RC1-supplement.pdf

Review of the manuscript “**Isotopic Signatures of Major Methane Sources in the Coal Seam Gas Fields and Adjacent Agricultural Districts, Queensland, Australia**” by Xinyi Lu et al.

Short summary of the manuscript

This paper presents results from campaigns of in-situ CH_4 mole fraction measurements and of air samplings for subsequent isotope analyses. The authors characterized carbon and hydrogen stable isotope signatures of various CH_4 sources in the Surat Basin, Australia and compared the values with those in previously reported literature.

General comment

This is a good piece of work showing 2-year campaign measurement results. Previously, Sherwood et al. (2017) compiled thousands of isotope signature data of various CH_4 sources, but availability of such data is still limited for some regions or source types. This study will be acknowledged for complement of the available dataset and for important information for isotope based top-down estimate of the Australian CH_4 emissions. This work is well within the scope of the journal and has significance in the study field. For publication of this manuscript, I would like to encourage the authors major revisions to consider my comments below.

Authors' response:

We thank the reviewer for placing the scientific value of this research in both the global and national context, and for the supportive comments and encouragement. Below we have addressed the constructive comments about the manuscript and highlighted where we have made revisions.

1. Representativeness of the isotope signatures presented in this study

This study presents isotope signatures of various sources in the Surat Basin. The results showed that the estimated isotope signatures of same source type sometimes differ from site to site. In such field studies, critically important is how representative the result is. Previous studies have inferred that $\delta^{13}C$ and δD signatures of CH_4 emitted from some sources vary considerably with time and space. I am very curious to discussion on how representative the isotope signatures obtained in this study are. Such discussion is crucial when the results are considered for constraints to the regional CH_4 budget. There are two points I can come up with. First, whether the set of air samples were collected from downwind of the major emission locations of the source. The higher fraction of emission at the location among the total emission is, the more representative the results would be. Second, how large variability among isotope signatures from a single source type is. For instance, the results indicate that isotope signatures of CH_4 of CSG origin vary by 5 ‰ in $\delta^{13}C$ and by 20 ‰ in δD, depending on sampling location/time. But the variability is much smaller for ground seeps in $\delta^{13}C$, which may suggest the source isotope signatures are relatively constant/uniform. Such discussion could be made not only from the results from the present study but also from those from the earlier studies (Table 1). I would like to see more enriched discussions about what we can learn about representativeness from this study and give some suggestions about better sampling strategy for a similar study in future. It could affect discussions in section 3.3, because distinctiveness of isotope signatures of different source types depends on this issue. For instance, some part of $\delta^{13}C$ and δD signatures overlap between fossil fuel and biogenic sources according to the Sherwood et al. (2017) database, but their global representative values are considered to be sufficiently different so that we can examine partition estimates for contributions of both sources to atmospheric CH_4 variations.

Authors' response:

We acknowledge the importance and challenges with quantifying how representative the presented isotopic signatures are.

With regards to "First, whether the set of air samples were collected from downwind of the major emission locations of the source.": we collected all air samples downwind of each source. A portion of the samples were collected close to centre line, and then additional samples towards the edge of the plume in order to maximise the spread of CH_4 mole fraction readings used in the Keeling regressions.

Regarding "Second, how large variability among isotope signatures from a single source type is.": the authors acknowledge that this is a challenge for studies of this nature. It would take considerable time and resources to collect multiple bag sets at multiple common sources. For this study we collected and analysed over 160 bag samples and attempted to characterise the isotopic signature of all major sources in the region. For export abattoirs (meat works) and piggeries, these are the first isotopic signatures reported for these sources in Australia, and for most other sources these are the first deuterium measurements.

We have modified the following sentences in the manuscript:

P23 L594 – L602: "[…] ~~Air samples for isotope analysis were collected from CH_4 plumes from various sources.~~ ~~The $\delta^{13}C_{CH4}$ and δD_{CH4} signatures of CH_4 emitted from CSG infrastructures, an open-cut coal mine, ground and river seeps, grazing cattle and feedlot, a piggery, a landfill, a wastewater treatment plant, two abattoirs with biogas plants and a small urban area were investigated.~~ We present the $\delta^{13}C_{CH4}$ isotopic signatures for 16 plumes and the δD_{CH4} isotopic signatures for 13 plumes, from the analyses of over 160 air samples. Despite the size of the data set, for many sources only a single isotopic signature has been determined. However, this single isotopic value represents the first recorded isotopic signature for some sources (e.g., abattoirs and piggeries) in Australia. Generally, the $\delta^{13}C_{CH4}$ and δD_{CH4} signatures determined from isolated plumes mapped during our 2018 and 2019 campaigns agree with values reported in the literature (Table 1 and Fig. 6). ~~Here we have reported the first recorded $\delta^{13}C_{CH4}$ isotopic signatures of a piggery, two abattoirs, and a wastewater treatment plant in Australia.~~ More investigations in Australia are needed for further characterisation of other sources, both those listed in the UNFCCC inventory classifications and natural. There is also a need for further studies to characterise the temporal and spatial variability of all sources, climatic and seasonal influences, and procedural repeatability. Ideally, further sampling should be undertaken in collaboration with the operators of each facility, so that samples can be collected closer to the source, removing all uncertainty in the origin of the CH_4. This study has made a contribution to the $\delta^{13}C_{CH4}$ and δD_{CH4} signatures from different sources in Australia and internationally […]"

2. Data analysis

The authors employ the Miller-Tans plot. I could not however understand advantage of the analysis over the traditional Keeling plot. Keeling plot assumes that the background atmosphere is constant over the time period of interest, and thus provides a much simpler framework and data interpretation. In contrast, as shown by Miller and Tans (2003), Miller-Tans plot is useful when one needs to assume that the background atmospheric condition varies with time at significant level of magnitude. To my understanding, Miller-Tans plot should be chosen only for special cases, where constant background cannot be assumed. From this point of view, the authors argument "The background air normally does not change during this period but using the Miller-Tans approach is a safeguard against any variability." (P11 L295) seems strange to me.

Not only for the original Keeling (1958) paper (cited in the manuscript), the authors might revisit Miller and Tans (2003) for different ways of use of the two plots. Pataki et al. (2003) might also help for limitation of the Keeling plot.

In the case where the authors continue use of the Miller-Tans plot, they should clearly present how the time-varying background mole fractions and delta values are given for individual data points. It is not presented explicitly in the current manuscript. I suppose that it would for instance call for on-site continuous measurements in the upwind. Miller and Tans (2003) applied curvefitting to their time-series CO_2 data, and similar examples for CH_4 were given by Umezawa et al. (2012).

Additional useful reference is Zobits et al. (2006), who investigated difference of source isotope signatures between Keeling and Miller-Tans plots and between ordinary square and geometric mean regressions. They found that, for same conditions, both plots return practically identical source isotope signatures. However, when the range of mole fraction is relatively small, geometric mean regression method could cause a bias in the estimated source signature. Since this study targets relatively wide range of mole fraction variation, I suppose such a bias is small, but the authors could examine with their data and/or justify validity of their regression approach. According to the text, the "Bayesian regression" used in this study seems to be similar to geometric mean regression that could cause a bias for small range of mole fraction. Please explain more to justify the analysis method.

In summary, there would be no difference in estimated source signatures from both plots if constant background is assumed. However, unless the reason why Miller-Tans plot is needed is clearly given, I see that the authors make the analytical methodology complicated without necessity. And it is not logically clear why they chose the regression method. I would like to suggest the authors to revisit previous studies carefully and rewrite the corresponding section.

Pataki, D. E. et al. (2003), The application and interpretation of Keeling plots in terrestrial carbon cycle research. Global Biogeochem. Cycles, 17(1), 1022, https://doi.org/10.1029/2001GB001850.

Umezawa, T. et al. (2012), Contributions of natural and anthropogenic sources to atmospheric methane variations over western Siberia estimated from its carbon and hydrogen isotopes, Global Biogeochem. Cycles, 26, GB4009, https://doi.org/10.1029/2011GB004232.

Zobits, J. M. et al. (2006), Sensitivity analysis and quantification of uncertainty for isotopic mixing relationships in carbon cycle research. Agricultural and Forest Meteorology, 136, 56–75, https://doi.org/10.1016/j.agrformet.2006.01.003.

Authors' response:

We acknowledge that we were not precise with our statement in P11 L295. We agree that using the Keeling plot method improves the clarity of the manuscript and we now use this method throughout the manuscript. Converting to the Keeling plot method only results in minor changes (many only in the third significant figure) to the determined isotopic values and does not alter any of the discussion or conclusions in the originally submitted manuscript. We have updated the sentences in Sect. 2.4 P11 L287 – L299, P12 L318 – L322 and substitute the Keeling plots for Miller-Tans plots for all sampled plumes in the Appendix A (Figs. A3–A7).

P11 L287 – L299: "The $\delta^{13}C_{CH4}$ and δD_{CH4} for CH_4 sources of each detected plume were determined using the ~~Miller–Tans~~ Keeling plot approach (~~Miller and Tans, 2003~~ Keeling, 1958; Pataki et al., 2003) shown in Eq. (1):

$$\delta_{(a)} = \left[CH_{4(b)}\right](\delta_{(b)} - \delta_{(s)}) * 1/\left[CH_{4(a)}\right] + \delta_{(s)} \qquad (1)$$

where $[CH_{4(b)}]$ and $\delta_{(b)}$ are the CH_4 mole fraction and $\delta^{13}C_{CH4}$ (or δD_{CH4}) of the background air, $[CH_{4(a)}]$ and $\delta_{(a)}$ are the CH_4 mole fraction and $\delta^{13}C_{CH4}$ (or δD_{CH4}) of the atmosphere and $\delta_{(s)}$ is the $\delta^{13}C_{CH4}$ (or δD_{CH4}) of the mean source, respectively. The ~~slope~~ intercept ($\delta_{(s)}$) of the linear regression between $\delta_{(a)}$ ~~$* [CH4(a)]$~~ and $1/[CH_{4(a)}]$ represents the isotopic signature of the source mixed in the background ambient air. The Keeling plot method requires the background air CH_4 mole fraction and isotopic signature to be constant during the period of observation. The time it takes to collect the 10 samples is approximately 30 minutes, and normally the background air composition does not change during ~~this~~ the period of sampling. ~~but using the Miller–Tans approach is a safeguard against any variability.~~ The mobile survey readings show that the background CH$_4$ mole fraction was stable in 2018 and 2019 daytime and nighttime surveys (Fig. A2), which supports this assumption. For each ~~Miller–Tans~~ Keeling data set the Bayesian linear regression line and credible interval (analogous to confidence interval) were determined using the PyMC3 Bayesian regression package (Salvatier et al., 2016). The regression methodology was selected based on the fact that there are bivariant correlated errors in both the x and y variables (e.g., Miller and Tans, 2003; Zazzeri et al., 2016) and the number of samples in each plume set was small (<= 10). Bayesian regression was used since it is a robust algorithm that balances uncertainty in both the x and y axis data (Jaynes and Crow, 1999), ~~and~~ it is suitable for small data sets (Baldwin and Larson, 2017)~~.~~, and it has been demonstrated to yield more reliable isotopic signatures at low mole fractions with low sample numbers (Zobitz et al., 2007).

P12 L318 – L322: "The Keeling plot results of CH$_4$ source signature calculations are listed in Table 2 and shown in Fig. 3. The ~~Miller–Tans~~ Keeling plots are shown in Figs. A~~1~~3–A~~5~~7 in Appendix A. ~~All~~ For each $\delta^{13}C_{CH4}$ (‰) and δD_{CH4} (‰) isotopic signature~~s~~ both the posterior standard deviation and the ~~are determined with~~ ~~uncertainties~~ credible interval ~~of ± 0.2 ‰ to ± 3.4~~ were determined. The variability in the ~~uncertainty~~ credible interval is primarily due to both the ~~sampling~~ sampled CH$_4$ mole fraction range and the number of data points used in the ~~Miller–Tans~~ Keeling plot analysis as shown in Fig. A8. ~~All δD_{CH4} (‰) signatures were determined with~~ ~~uncertainties of ± 0.2 ‰ to ± 4.2~~. ~~The largest uncertainty was associated with the mixed urban emissions due to the limited range of sampled CH$_4$ mole fractions.~~"

We have also updated the caption of Table 2 as follows:

P13 L329: "Table 2: CH$_4$ source signature results for plumes sampled in the Surat Basin 2018 and 2019 campaigns. CH$_4$ excess over background (ppm) for the samples that were used to calculate the source signature. $\delta^{13}C_{CH4}$ (‰) and δD_{CH4} (‰) are reported along with the Bayesian posterior distribution mean, standard deviation and 95 % credible interval (in brackets). NA: not applicable."

Within the bounds of the credible interval (the Bayesian measure of uncertainty) the derived isotopic signatures are similar, and the overall interpretation of the results does not alter. Throughout the text we have replaced "uncertainty" with the Bayesian statistical terminology "credible interval" to convey the use of Bayesian statistics for all regression analyses.

The determination of the line of best fit for the Keeling plots is a generic regression problem. It is well established in the statistical analysis literature that when there is error in both the x and y variables the use of ordinary least squares is not appropriate. This is discussed in Miller and Tans (2003). The authors have used in numerous publications the bivariant correlated error with scatter (BCES) algorithm (Akritas and Bershady, 1996); for example, refer to the cited ACP publication Zarreri et al. (2016). On the GitHub web resources page for the BCES python scripts there is a discussion on the advantages of Bayesian linear regression over the BCES algorithm. https://github.com/rsnemmen/BCES.

The reviewer has pointed to the study of Zobitz et al. (2006) for justification to use ordinary least squares regression. We would like to highlight that for a small sample size Keeling plot, Zobitz et al. (2007) used Bayesian regression (Fig. 2 in that paper) and demonstrated that it performed better than ordinary least squares regression for small data sets.

Bayesian linear regression is now commonly used in many fields of science where there is a need to characterise parameter uncertainty for regression of small sample size data sets, when there is the likelihood of outliers and there is error in both the x and y variables. The authors feel it is beyond the scope of this manuscript to do a regression methodology comparison study for fitting Keeling and Miller–Tans regression lines, especially when Bayesian regression is now commonly used, is available in many mathematical packages, and there are both R and Python libraries on GitHub.

For this manuscript we have stayed with using Bayesian regression, especially since Zobitz et al. (2007) established that Bayesian regression is a robust algorithm for Keeling plot analyses. We also note that there is no significant difference between the isotopic signatures determined for all samples using either the Keeling or Miller–Tans methods.

3. Description of the instrument performance

The authors should present their performance tests of the instruments (Los Gatos and Picarro) made before the campaigns. It seems that the current descriptions rely on information provided by the product companies only, which is performance of their standard products at shipment from factory, but we know that there are differences among products and importantly that stability of those instruments (e.g. during shipment, repetitive power on/off, change in temperature/humidity) has not been well established. It is important to show readers sufficient key information on validity of their measurements, independent from that from the provider.

Authors' response:

In the manuscript text below and Appendix A (Fig. A1) we now provide the infield performance data for both the UNSW Sydney LGR-UGGA and Picarro G2201-i CRDS units. The Picarro G2201-i CRDS and LGR-UGGA units were used only to locate the plumes, and we used the Picarro G2201-i CRDS CH_4 mole fraction data for checking if the bags leaked when the samples were shipped between UNSW Sydney and RHUL. None of the Keeling plot results use the UNSW Sydney Picarro data. We presented only a low-resolution image of the plume positions, to convey the scale of the project, the frequency of major plumes, and the order of magnitude of enhancement in the CH_4 mole fraction readings at the sampling locations. We acknowledge that changes in temperature and humidity affect both concentration and isotopic measurements using laser spectrometers. It is for this same reason that data used for Keeling plot analysis was obtained under laboratory conditions using a well-established analytical technique (IRMS).

We also added the following text in the manuscript:

P9 L245: "[…] The in-field standard deviations for mean CH_4 mole fraction measurements of the reference standard across all days were 4.9 ppb (2018) and 9.6 ppb (2019) for

LGR-UGGA and 5.3 ppb (2018) for Picarro G2201-i CRDS. This repeatability is better than reported in Takriti et al. (2021)."

P9 L254: "[...] purposes. In 2018 the root-mean-square error (RMSE) between the University of New South Wales (UNSW Sydney) Picarro 2201-i CRDS and the RHUL Picarro G1301 CRDS (detailed below) was 0.437 (ppm; Fig. A1 (a)) and in 2019 the RMSE between the UNSW Sydney Picarro 2201-i CRDS and the Institute for Marine and Atmospheric research Utrecht (IMAU) continuous-flow isotope ratio mass spectrometry (CF-IRMS) (detailed below) was 0.232 (ppm; Fig. A1 (b))

The following reference is added:

Takriti, M., Wynn, P. M., Elias, D. M. O., Ward, S. E., Oakley, S. and McNamara, N. P.: Mobile methane measurements: Effects of instrument specifications on data interpretation, reproducibility, and isotopic precision, Atmos. Environ., 246, 118067, https://doi.org/10.1016/j.atmosenv.2020.118067, 2021.

Specific Comments

P1 L14: "The use of…" This sentence needs rewriting. It is not clear how the authors consider difference of the three verbs. I think that (use of) $\delta^{13}C$ and δD can "help us" identify a specific source "if potential sources are all characterized in $\delta^{13}C$ and δD signatures."

Authors' response:

We thank the Referee for this suggestion. To clarify the wording the sentence has been rephrased:

P1 L14: "The characterisation of carbon ($\delta^{13}C$) and hydrogen (δD) stable isotopic composition of CH_4 can help distinguish between specific emissions of CH_4 […].

P1 L16: It is not clear how different "discriminate" is from for instance "distinguish between" in the earlier sentence.

Authors' response:

To clarify the wording the sentence has been rephrased:

P1 L16: "[…] This research examines whether dual isotopic signatures of CH_4 can be used to distinguish between sources of CH_4 in the Surat Basin."

P2 L40: "e.g." should be added before "Nisbet et al. 2020", otherwise additional reference that cover "greenhouse gases" is needed. I think the reference is for CH_4 only.

Authors' response:

Agreed and revised to the following:

P2 L40: "to anthropogenic industrial and agricultural activities (e.g., Nisbet et al., 2020) […]"

P2 L60: The CH_4 increase over the industrial era and stagnation during the early 2000s are phenomena with totally different time scales.

> Authors' response: Agreed and revised to the following:
>
> P2 L60 – L61: "[…] ~~The CH_4 mole fraction has been increasing since industrialisation, with~~ The CH_4 mole fraction has increased by 160 % since industrialisation. The rate of increase is typically 0.4 to 14.7 ppb per year, although there was a short pause in the growth rate of atmospheric CH_4 between 1999 and 2006 (Schaefer et al., 2016; Dlugokencky, 2021) […]"
>
> The following reference is added:
>
> Dlugokencky, E.J.: Annual Increase in Globally-Averaged Atmospheric Methane, NOAA/GML, https://www.esrl.noaa.gov/gmd/ccgg/trends_ch4/, last access: 21 April 2021.

P3 L65: There are indeed many references that addressed different time phases of the atmospheric CH_4 increase. First, I would like to suggest the authors to cite references that substantially contributed to the present study only. Did all these references contributed equally to the present study? Second, as written in the sentence, such debate has continued over the last decades, while the references are all relatively new. It might give wrong impression that the problem is new. Some "old" but key references, for instance Steele et al. (1992), Dlugokencky et al. (1998), Bousquet al. (2006), Simpson et al. (2012) and others, could be considered. Additionally, a recent study Chandra et al. (2021) present conclusion similar to that by Jackson et al. (2020). That said, choice of references is up to the authors.

Steele, L., Dlugokencky, E., Lang, P. et al. Slowing down of the global accumulation of atmospheric methane during the 1980s. Nature 358, 313–316 (1992). https://doi.org/10.1038/358313a0.

Dlugokencky, E., Masarie, K., Lang, P. et al. Continuing decline in the growth rate of the atmospheric methane burden. Nature 393, 447–450 (1998). https://doi.org/10.1038/30934.

Bousquet, P., Ciais, P., Miller, J. et al. Contribution of anthropogenic and natural sources to atmospheric methane variability. Nature 443, 439–443 (2006). https://doi.org/10.1038/nature05132.

Simpson, I., Sulbaek Andersen, M., Meinardi, S. et al. Long-term decline of global atmospheric ethane concentrations and implications for methane. Nature 488, 490–494 (2012). https://doi.org/10.1038/nature11342.

Chandra, N., P. K. Patra, J. S. H. Bisht, et al. Emissions from the Oil and Gas Sectors, Coal Mining and Ruminant Farming Drive Methane Growth over the Past Three Decades. Journal of the Meteorological Society of Japan (2021). https://doi.org/10.2151/jmsj.2021015.

Authors' response:

We agree with the Referee's comment. Indeed, some key references in the past have substantially contributed to the current study of CH_4 increase. We have therefore made the following changes:

P3 L65 – L67: "[…] between agriculture versus fossil fuels (Bousquet et al., 2006; Chandra et al., 2021; ~~Hausmann et al., 2016;~~ Jackson et al., 2020; Kirschke et al., 2013; Nisbet et al., 2014, 2016, 2019; Rice et al., 2016; Rigby et al., 2017; ~~Schaefer et al., 2016;~~ Schwietzke et al., 2016; Turner et al., 2017; Worden et al., 2017) […]"

The following references will be added to the updated manuscript:

Bousquet, P., Ciais, P., Miller, J. B., Dlugokencky, E. J., Hauglustaine, D. A., Prigent, C., Van Der Werf, G. R., Peylin, P., Brunke, E. G., Carouge, C., Langenfelds, R. L., Lathière, J., Papa, F., Ramonet, M., Schmidt, M., Steele, L. P., Tyler, S. C. and White, J.: Contribution of anthropogenic and natural sources to atmospheric methane variability, Nature, 443(7110), 439–443, https://doi.org/10.1038/nature05132, 2006.

Chandra, N., Patra, P. K., Bisht, J. S. H., Ito, A., Umezawa, T., Saigusa, N., Morimoto, S., Aoki, S., Janssens-Maenhout, G., Fujita, R., Takigawa, M., Watanabe, S., Saitoh, N. and Canadell, J. G.: Emissions from the Oil and Gas Sectors, Coal Mining and Ruminant Farming Drive Methane Growth over the Past Three Decades, J. Meteorol. Soc. Japan. Ser. II, 2021–015, https://doi.org/10.2151/jmsj.2021-015, 2021.

The following reference will be deleted from the updated manuscript:

~~Hausmann, P., Sussmann, R. and Smale, D.: Contribution of oil and natural gas production to renewed increase in atmospheric methane (2007–2014): top–down estimate from ethane and methane column observations, Atmos. Chem. Phys., 16(5), 3227–3244, doi:10.5194/acp-16-3227-2016, 2016.~~

P3 L69: "natural fossil fuel source" looks strange. All fossil fuels are of natural origin in nature. The difference is just emission takes place by nature or by human. Etiope and colleagues have used the term "geological". Please rephrase.

Authors' response: Agreed and revised to the following:

P3 L69: "although this result contradicts emission estimates on the size of ~~natural~~ geological ~~fossil fuel~~ CH_4 sources (Etiope et al., 2019) […]"

P3 L69: What is the current global fraction of emissions from unconventional sources in the total fossil fuel related CH_4 emissions?

Authors' response:

The authors agree that information on the current global fraction of emissions from unconventional sources in the total fossil fuel related CH_4 emissions is important. To help the reader to understand this issue, a sentence was added to P3 L74:

P3 L74: "CH_4 emissions (Lan et al., 2019). It is estimated that around 14 % of total fossil fuel CH_4 emissions are from unconventional sources in 2020 (IEA, 2021) […]"

The following reference will be added to the updated manuscript:

IEA: Methane Tracker Database, IEA, Paris: https://www.iea.org/articles/methane-tracker-database, last access: 8 April 2021, 2021.

P4 L121: Same comment as that for P3 L65.

Authors' response:

We have made the following changes:

P4 L120 – L122: "(Beck et al., 2012; Fisher et al., 2017; France et al., 2016; Lowry et al., 2020; McNorton et al., 2018; Nisbet et al., 2016, 2019; Rice et al., 2016; Rigby et al., 2017; Röckmann et al., 2016; ~~Schaefer et al., 2016~~; Schwietzke et al., 2014, 2016; Tarasova et al., 2006; ~~Turner et al., 2017; Worden et al., 2017~~) […]"

P8 L219: What is the actual precision evaluated by the study team and expected during the campaign? Please see my earlier comment.

Authors' response:

We thank the Referee for the comment. Please refer to our response for General comment 3.

P9 L225: The same question as that for P8 L219. The information here seems to be identical to those on the Data Sheet provided on the Picarro website

(https://www.picarro.com/support/library/documents/g2201i_analyzer_datasheet). These are general instrument performance when it is shipped from factory. I suppose that the study team did not use the instrument as delivered but carried out series of evaluations before the campaign. The authors should present those results that better represent the actual performance during the campaign.

Authors' response:

We thank the Referee for the comment. Please refer to our response for General comment 3.

P9 L231: The more details of the time lag correction should be presented. How did you estimate the time lag? Is it time dependent or constant? How long is it on average?

Authors' response:

We have made the following changes:

P9 L231 – L233: "[…] ~~To correct for the time lag between GPS location and CRDS recorded data caused by slow flow rate and inlet tube length (~ 2.5 m), we adjusted the time stamp of CH_4 mole fraction and $\delta^{13}C_{CH4}$ readings based on observed delay of the~~

~~analyser response to a source.~~ Using the standard air, we determined the time lag between the real-time GPS location reading and the display of mole fraction reading on the Picarro G2201-i CRDS to be 3 min and 40 s. Using this timing offset, we adjusted the time stamp for the analyser data."

P9 L243: Please describe the value explicitly. What is the exact value and uncertainty measured by another laboratory? I believe the measurement was made by INSTAAR, not NOAA/GML.

Authors' response:

Our intention was to demonstrate that the RHUL $\delta^{13}C_{CH4}$ measurement of the calibration air provided by CSIRO was in good agreement with the flasks collected at Cape Grim around the same time. To clarify the wording the sentence has been rephrased:

P9 L241 – L244: "[…] RHUL also measured the CH_4 mole fraction of the calibration gas (1801.2 ± 0.5 ppb), ~~which agrees closely with the value from CSIRO, demonstrating minimal handling or gas exchange issues with the FlexFoil bags.~~ The isotope value measured by RHUL (−47.2 ± 0.05 ‰) also closely resembles the value from flasks (−47.2 ± 0.04 ‰, mean ± standard deviation for 12 flasks collected) collected at Cape Grim and measured at the ~~NOAA Global Monitoring Laboratory~~ Institute of Arctic and Alpine Research (INSTAAR), University of Colorado (White et al., 2018) […]"

P9 L247: Was the driving speed adjusted specifically for the different instruments (e.g. flow rate)? If so, additional information will help readers.

Author's response: Please refer to the response to General Comment 3.

P10 L267: Here the authors refer to the WMO X2004A scale traceable by the gas cylinders provided by NOAA. In the section before, they wrote "WMO scale" only. Reading these sentences, I cannot be sure that the mole fraction values from CSIRO and RHUL are on the identical scale. Please sort this out so that use of one single measurement scale is clear throughout the paper. Though the principal methodology is still valid, since the original WMO X2004 scale was updated to WMO X2004A in 2015, the reference Dlugokencky et al. (2005) no longer represents the current WMO scale exactly. I would suggest to additionally cite the NOAA website (https://www.esrl.noaa.gov/gmd/ccl/ch4_scale.html) or the latest WMO GAW Report No. 255 (https://library.wmo.int/index.php?lvl=notice_display&id=21758#.YE7BLS9h0UE). It should be somewhere noted that the current WMO scale cover up to ~5900 ppb and many measurements presented in this study are calculated by extrapolation of the scale. The abbreviation "NOAA" appeared earlier.

Authors' response:

We apologise for the unclear description of the calibration scale. The above-mentioned calibration air (appeared in P9 L235 – L239) was provided by CSIRO but measured by RHUL to link analysers to the same WMO X2004A scale of that at RHUL. We have made the following changes for clarification:

P9 L236 – L239: "by Commonwealth Scientific and Industrial Research Organisation (CSIRO) ~~with a CH_4 mole fraction of 1800.6 ± 0.7 ppb and $\delta^{13}C_{CH4}$ of −47.2 ‰. The CH_4 mole fraction was measured in CSIRO's Global Atmospheric Sampling Laboratory (GASLAB) in Aspendale (Francey et al., 2003) and referenced to the World Meteorological Organization (WMO) scale (Dlugokencky et al., 2005).~~ The calibration gas was ~~also~~ placed into 3 litre SKC FlexFoil PLUS sample bags (SKC Inc., USA) for shipping and analysed at the greenhouse gas laboratory of Royal Holloway, University of London (RHUL) to determine the $\delta^{13}C_{CH4}$ for the calibration air (−47.2 ± 0.05‰). RHUL also measured the CH_4 mole fraction of the calibration gas (1801.2 ± 0.5 ppb).~~, which agrees closely with the value from CSIRO, demonstrating minimal handling or gas exchange issues with the FlexFoil bags~~[…]"

P10 L267 – L268: "calibrated to the WMO X2004A scale using NOAA (National Oceanic and Atmospheric Administration) air standards (Dlugokencky et al., 2005; Fisher et al., 2006, 2011; WMO 2020) […]"

The following reference will be added to the updated manuscript:

WMO: 20th WMO/IAEA Meeting on Carbon Dioxide, Other Greenhouse Gases and Related Measurement Techniques (GGMT-2019), Jeju Island, South Korea, 2–5 September 2019, GAW Report No. 255, 140 pp., https://library.wmo.int/inde x.php?lvl=notice_display&id=21758#.YJzyYmYzbUI, 2020.

P10 L276: I would suggest a sentence like "For the subsequent IRMS measurement, CH_4 in sample air in most bags were preconcentrated for 10 minutes at…, but that in samples with CH_4 mole fraction larger than 6 ppm reported by RHUL were processed for shorter time in order to…" if I understand correctly. I suppose that "sampled" in the original sentence is not just collecting air but preconcentration of CH_4 from sample air, as written in the following sentence.

Authors' response:

That is correct. To clarify we have rephrased the sentence to the following:

P10 L276: "[…] ~~Most bags were sampled~~ For the subsequent IRMS measurement, the CH_4 in air from most bags were preconcentrated for 10 minutes at a flow rate of 6 mL min^{-1} for δD_{CH4} and 4 mL min^{-1} for $\delta^{13}C_{CH4}$, but for samples reported by RHUL that had a CH_4 mole fraction larger than 6 ppm they were ~~sampled~~ processed for a shorter time in order to extract a quantity of CH_4 similar to the reference air.

P10 L283: What does "UNSW" stands for?

Authors' response:

UNSW is the abbreviation for The University of New South Wales, Sydney, Australia. The official abbreviation for the university is UNSW Sydney. We have defined the abbreviation in the author listing and change UNSW to "UNSW Sydney" throughout the text.

P11 Section 2.4: Please see my earlier comment.

Authors' response: Please refer to our response for General comment 2.

P11 Section 3.1: More than half of sentences of this paragraph are for explaining the switch from daytime to nighttime sampling. I do not think the title of the section represent the content well. A problem of nighttime samplings might be darkness, which makes visible identification of the source difficult. I guess it might have been discussed when planning the campaigns. How did you overcome this problem? I am also curious to the similar mapping plots for $\delta^{13}C$ of CH_4. Spatial variability of $\delta^{13}C$ corresponding to those in the CH_4 mole fraction in Fig. 2 is also valuable information for readers especially who consider plan of similar type of field surveys.

Authors' response:

The authors agree that a more representative title is needed. We have made changes as follows:

P11 L301: "**3.1 Regional plume mapping and the benefits of sampling at nighttime**"

P11 L306: "In 2018, we did not detect plumes from coal mines, river seeps, abattoirs, piggeries or WWTP, thus we shifted our focus from daytime surveying […]"

Regarding the problem locating sources when doing nighttime sampling, most facilities are well lit. We added the following sentence:

P11 L313: "plots and minimises the uncertainties of the derived isotopic source signatures. As part of developing an inventory (Neininger et al., in review) in the region, all major CH_4 sources were located and were georeferenced to guide nighttime sampling. Also, most facilities were well lit, which assisted with source identification. The contrast in the magnitude of the CH_4 mole fraction […]"

The following reference has been added:

Neininger, B.G., Kelly, B.F.J., Hacker, J.M., Lu, X., Schwietzke, S., Coal seam gas industry methane emissions in the Surat Basin, Australia: Comparing airborne measurements with inventories, Phil. Trans. R. Soc. A., in review.

Regarding "similar mapping plots for $\delta^{13}C$ of CH_4": it was never the goal to produce isotope maps, the goal was to find the CH_4 plumes. We used the Picarro G2201-i CRDS for only a small portion of the survey when the LGR-UGGA failed. Only a small portion of the complete mole fraction survey would have isotope data from Picarro G2201-i CRDS, which is not sufficient to produce a similar map.

P11 L316: While the nighttime campaign detected more spikes with high CH_4 mole fractions, there are several peaks with comparable magnitude of CH_4 spikes (> 10 ppm) even in the daytime campaign. How are they explained? It would be helpful if you could add labels for key sources in Figure 1. I tried to compare Figs 1 and 2 but found it difficult to find corresponding locations of the peaks exactly.

Authors' response:

We cannot provide a detailed answer because we did not analyse the flux of each source. The CH_4 mole fraction at the point of sampling is a complex function of source strength, distance to the source, wind speed, wind direction, surface roughness, temperature, uplift rate, among other variables. We have placed source numbers on Fig. 1 in line with Table 2 and modified the caption of Fig. 1 as follows:

P8 L213: "Queensland (Inset map data: Australian Government (2020)), Administrative Boundaries © Geoscape Australia). The positions of the sampled CH_4 plumes are numbered 1 through 16."

P12 Section 3.2: Before going into results of source signatures, it would be good to show some selected examples of the observed Miller-Tans (or Keeling) plots from both campaigns. It could be done as Figure 3, not appendix figures. Such figures could represent how closely the observed $\delta^{13}C$ varied with the observed CH_4 mole fraction, which is key information that support validity of the characterization analysis for source isotope signatures presented in this study. Also, from this point of view, I would prefer Keeling plot if possible, where magnitude of the observed $\delta^{13}C$ variations is obvious on the vertical axis. I am curious to how largely $\delta^{13}C$ varied in the plume air of different origins.

Authors' response:

We believe that the required details are succinctly summarised for all sources in Table 2 to inform a reader on "how largely $\delta^{13}C$ varied in the plume air of different origins". In updated Table 2 all derived $\delta^{13}C$ and δD values are reported, along with the credible interval now added for those parameters.

Keeling plots have also been provided now in the Appendix A (Figs. A3–A7) and cross referenced in the caption of Table 2.

P12 L319: What is the "uncertainties" of the estimated source signatures? Please describe explicitly. It could be presented in section 2.4.

Authors' response: Please refer to our response to General comment 2.

P12 L321: If so, it could be possible to see a characteristic feature when the estimated uncertainties are plotted versus range (or maximum) of the observed CH_4 mole fractions for individual plumes. Perhaps the authors could infer how much elevation in CH_4 mole fraction is desired for precise estimation of source isotope signature based on plume surveys like this study.

Authors' response:

We thank the reviewer for this suggestion. The precise estimation of source isotope signatures depends on several factors such as maximum CH_4 mole fractions observed, number of samples collected, distance from source and wind direction. We have presented the dependency between 95 % credible interval range of $\delta^{13}C$ (a) and δD (b) derived from Keeling plot method and number of samples and measured CH_4 mole fraction range from the corresponding measured sources in Fig. A8 in Appendix A. The result agrees well with previous studies (e.g., Hoheisel et al., 2019; Takriti et al., 2021).

With respect to the measurement systems, we have added the following sentence:

P10 L285: "[…] Due to the high precision of the RHUL GC-IRMS measurements of < 0.05 ‰ for $\delta^{13}C$, the IMAU IRMS measurements of < 0.1 ‰ for $\delta^{13}C$ and < 2 ‰ for δD, reliable source signatures can usually be derived for elevations of 100–200 ppb above the background"

P13 Table 2: A number for each plume could be assigned. It would help readers to find a line in the Table corresponding to texts in the following sections.

Authors' response:

We thank the Referee for making this use recommendation. We have assigned a number for each plume in Table 2 and added the plume number when referencing the plume in the manuscript.

P17 L424: "calm to light wind conditions" What is the wind speed at the observation time? There are similar subjective expressions also at other places. It is considered that degree of accumulation of CH_4 emitted from a nearby source is dependent on wind speed as the authors also explains in this manuscript. For example, constant 5 m/s wind brings influence of 300 m upwind source with a 1 minute delay, and we would collect footprint of 18 km upwind in an hour. It is therefore important to present an exact number to convince predominance of a nearby source. If no on-site measurement is available, the authors might look for data from a nearby weather station.

Authors' response:

Calm to light wind descriptions was the official Australian Bureau of Meteorology wind speed description at the time of sampling – 0 to 14 km^{-1}.

The speed has been added in brackets after the description in the manuscript:

P17 L424: "plumes near the Chinchilla weir and measured CH_4 mole fractions as high as 18 ppm in calm to light wind conditions (0–14 km h^{-1}) […]"

P18 L441: I am confused by this sentence. I understand that this study aims at characterizing isotope signatures of known sources, but here it seems the author tries to infer contributing sources based on isotope signature.

Authors' response:

The CH_4 isotope signatures of Abattoir A and B were calculated to represent the abattoir facilities instead of a single source. We have updated in the manuscript to highlight that the CH_4 isotope signatures presented in this study are either for a single source (e.g., venting pipeline, raw water pond) or a facility with several potential CH_4 sources (e.g., abattoirs, feedlots, and piggeries).

We have also made the following changes to P18 L441:

P18 L441 – L442: "integrated feedlot and processing plant.~~ The measured $\delta^{13}C_{CH4}$ signature suggests that the plume sampled is most likely associated with waste emissions.~~"

P18 L446: As far as I understand, a single source with $\delta^{13}C$ signature of -44.3±0.3 ‰ is not identified but interpreted as mixture of several potential sources. It is not clear that why the source signature is compared to those of a single source from different regions. Given that every isotope signature of the four potential sources is unknown, it is also difficult to infer possible contributions.

Authors' response:

We agree that the potential sources of the mixed urban emissions are unknown, and it is not suitable to be compared with other single sources or single facilities. We therefore removed the Mixed urban emissions from Table 2 and Fig. 3, deleted Sect. 3.2.9 and the plots in Appendix and the following sentence in the manuscript:

P7 L193 – L196: "~~Each town centre has many potential sources of CH_4 including, but not limited to, leaking gas bottles, instant hot water systems, rubbish bins, vehicles and domestic wood fires (which are common in the region). To characterise these collective emissions, samples were collected from a typical residential area in Dalby, which has a population of approximately 12,000 (Australian Bureau of Statistics, 2016).~~"

P12 L321 – L322: "~~The largest uncertainty was associated with the mixed urban emissions due to the limited range of sampled CH_4 mole fractions.~~"

P19 L467: Same comment as that for P18 L441. The authors try identification of sources or separate contributions of sources, but it contrasts to this study's purpose of characterization of individual sources. I was therefore confused by impression that the objective change from section to section.

Authors' response: Please see the response to P18 L441.

P19 L479ff: Chang et al. (2019) suggested that $\delta^{13}C_{CH4}$ from ruminants correlates with $\delta^{13}C$ of the diet as follows: $\delta^{13}C_{CH4} = 0.91\times\delta^{13}C_{diet} - 43.49$. Could it be possible to check whether the present results are consistent with this equation? If the above equation is roughly valid for this study, $\delta^{13}C$ signature of the diet would be around -20‰, which lies between $\delta^{13}C$ of C3 and C4 plants. Is any information on the $\delta^{13}C$ of the diet available?

Chang et al. (2019) Revisiting enteric methane emissions from domestic ruminants and their $\delta^{13}C_{CH4}$ source signature, Nature Communications, https://doi.org/10.1038/s41467-01911066-3.

Authors' response:

We do not have the required diet information to do this calculation. No edit was made.

P20 Section 3.2.6: What is the likely production process of CH_4 in the piggery?

Authors’ response:

The possible production process of CH_4 in the piggery was introduced in P7 L177 – L180.

P21 L539: According to Figure 6, ruminants in Australia show biomodal $\delta^{13}C$ signature distribution, while samples collected for cattle in this study show values at depleted side only.

Authors’ response:

The $\delta^{13}C_{CH4}$ signature of cattle emitted CH_4 varies depending on many factors such as geographical location, diet (C3 or C4 plant) and breed of the animal (Hook et al., 2010). In Australia, cattle are hosted in different states with different geographical locations thus have varying diets. These factors could possibly explain the bimodal $\delta^{13}C_{CH4}$ signature distribution from limited data available. Further studies are also important to better understand the $\delta^{13}C_{CH4}$ signature of cattle emitted CH_4 from cattle in Australia. No edit was made.

P21 Section 3.3: When we consider use of $\delta^{13}C$ and δD of CH_4 as constraints to the regional (e.g. Surat Basin) budget of CH_4, critical is the representativeness of individual source isotope signature. In this regard, it is good that some types of the sources in the region (e.g. Ground and river seeps, abattoir) showed good agreement within narrow isotope signature ranges between campaigns in different years, suggesting that source isotope signatures vary a little e.g. well representative. In contrast, some sources showed larger differences between campaigns or locations, suggesting that source isotope signatures could vary with time and/or space. It is therefore still uncertain that how representative the source isotope signatures presented in this study are at regional scale. To overcome this issue, one needs more frequent and numerous surveys, which would be highly challenging. Otherwise, a bit more zoomed-out scale study so that one can capture outflow of mixture air from the entire source unit (not source point to point) might help. I would like to suggest the authors to add discussions on how representative the source signatures presented in this study could be considered and on possible future sampling strategies to better comprehend isotope signatures of various sources in the region.

Authors’ response: Please see the response to General Comment 1.

Technical Comments

P2 L43: “insights” to “data”. If the authors have something else, please clarify.

Authors’ response: Agreed and revised to the following:

P2 L43: “in conjunction with other data. While ethane measurements have been used […]”

P2 L48: “coal seam gas” to “CSG”.

Authors’ response: Agreed and revised to the following:

P2 L48: “largest CSG fields is co-located with large scale cattle feedlots […]”

P4 L108: “n.d.” to “2016”

Authors’ response: Agreed and revised to the following:

P4 L108: “[…] because it is often co-emitted in fossil fuel emissions (Conley et al., 2016; Dlugokencky et al., 2011; Lowry et al., 2020; Smith et al., 2015) […]”

P4 L130: “coal seam gas” to “CSG”.

Authors’ response: Agreed and revised to the following:

P4 L130: “Here we present mobile CH_4 surveys in the CSG fields in southeast […]”

P5 L133: “chemistry” to “signature”.

Authors’ response: Agreed and revised to the following:

P5 L133: “database on the isotopic signature of CH_4 sources in Australia […]”

P6 L152: “coal seam gas” to “CSG”

Authors’ response: Agreed and revised to the following:

P6 L152: “[…] All the CSG in the Surat Basin […]”

P8 L216: “coal seam gas” to “CSG”

Authors’ response: Agreed and revised to the following:

P8 L216: “the main roads throughout the major CSG and agricultural regions of the Surat Basin […]”

P9 L243: “closely” to “well”

Authors’ response: Agreed and revised to the following:

P9 L243: “agrees well with the value from CSIRO […]”

P9 L252: “coal seam gas” to “CSG”

Authors’ response: Agreed and revised to the following:

P9 L252: “samples were collected from 16 major sources in the Surat Basin CSG fields […]”

P11 L310: “light” to “weak”

Authors’ response: Agreed and revised to the following:

P11 L310: “[…] at night during weak to moderate wind conditions […]”

P23 L594: "coal seam gas" to "CSG"

Authors' response: Agreed and revised to the following:

P23 L594: "eastern Surat Basin CSG fields in Queensland, Australia […]"

P24 L614: "coal seam gas" to "CSG"

Authors' response: Agreed and revised to the following:

P24 L614: "signatures from CSG sources overlap with signatures expected from landfills […]"

References

Akritas, M. G. and Bershady, M. A.: Linear Regression for Astronomical Data with Measurement Errors and Intrinsic Scatter, Astrophys. J., 470, 706, https://doi.org/10.1086/177901, 1996.

Hoheisel, A., Yeman, C., Dinger, F., Eckhardt, H. and Schmidt, M.: An improved method for mobile characterisation of $\delta^{13}CH_4$ source signatures and its application in Germany, Atmos. Meas. Tech., 12(2), 1123–1139, https://doi.org/10.5194/amt-12-1123-2019, 2019.

Hook, S. E., Wright, A. D. G. and McBride, B. W.: Methanogens: Methane producers of the rumen and mitigation strategies, Archaea, 2010, https://doi.org/10.1155/2010/945785, 2010.

Miller, J. B. and Tans, P. P.: Calculating isotopic fractionation from atmospheric measurements at various scales, Tellus B, 55(2), 207–214, https://doi.org/10.1034/j.1600-0889.2003.00020.x, 2003.

Takriti, M., Wynn, P. M., Elias, D. M. O., Ward, S. E., Oakley, S. and McNamara, N. P.: Mobile methane measurements: Effects of instrument specifications on data interpretation, reproducibility, and isotopic precision, Atmos. Environ., 246, 118067, https://doi.org/10.1016/j.atmosenv.2020.118067, 2021.

Zazzeri, G., Lowry, D., Fisher, R. E., France, J. L., Lanoisellé, M., Kelly, B. F. J., Necki, J. M., Iverach, C. P., Ginty, E., Zimnoch, M., Jasek, A. and Nisbet, E. G.: Carbon isotopic signature of coal-derived methane emissions to the atmosphere: from coalification to alteration, Atmos. Chem. Phys, 16, 13669–13680, https://doi.org/10.5194/acp-16-13669-2016, 2016.

Zobitz, J. M., Burns, S. P., Ogée, J., Reichstein, M. and Bowling, D. R.: Partitioning net ecosystem exchange of CO2: A comparison of a Bayesian/isotope approach to environmental regression methods, J. Geophys. Res. Biogeosciences, 112(G3), https://doi.org/10.1029/2006JG000282, 2007.