Review of the manuscript "**Isotopic Signatures of Major Methane Sources in the Coal Seam Gas Fields and Adjacent Agricultural Districts, Queensland, Australia**" by Xinyu 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.

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.

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 curve-fitting 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.

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.

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) δ^{13}C and δD can “help us” identify a specific source “if potential sources are all characterized in δ^{13}C and δD signatures.”

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

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.

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

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.2021-015.

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.

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

P4 L121: Same comment as that for P3 L65.

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

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.

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?

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.

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

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 principle 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.

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.

P10 L283: What does "UNSW" stands for?

P11 Section 2.4: Please see my earlier comment.

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 Figure 2 is also valuable information for readers especially who consider plan of similar type of field surveys.

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.

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.

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

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.

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.

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.

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.

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.

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.

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/s41467-019-11066-3.

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

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.

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.

Technical Comments

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

P2 L48: “coal seam gas” to “CSG”.

P4 L108: “n.d.” to “2016”

P4 L130: “coal seam gas” to “CSG”.

P5 L133: “chemistry” to “signature”.

P6 L152: “coal seam gas” to “CSG”

P8 L216: “coal seam gas” to “CSG”

P9 L243: “closely” to “well”

P9 L252: “coal seam gas” to “CSG”

P11 L310: “light” to “weak”

P23 L594: “coal seam gas” to “CSG”

P24 L614: “coal seam gas” to “CSG”