Atmospheric Chemistry and Physics Discussions

Atmos. Chem. Phys. Discuss., referee comment RC1
https://doi.org/10.5194/acp-2021-76-RC1, 2021

Reply by the Authors to "Comment on acp-2021-76"

Anonymous Referee #2

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-RC2, 2021

General comments:
In this manuscript, Lu et al. present mobile atmospheric methane measurements conducted in 2018 and 2019 and subsequent laboratory analyse of the δC and δD in CH_4 signature of 17 methane sources in the Surat Basin. During the campaigns, mobile GHG analysers are used to identify emission plumes of different important CH_4 sources and whole-air samples taken within those plumes are later analysed in the lab by suitable means. The results are then compared with previous studies from Australia and globally. The authors also highlight the added value of double isotope analysis, i.e., δD and δC in CH_4.

Overall, the manuscript is well written and nicely structured, which makes it easy to follow. The issue of source apportionment of anthropogenic and natural methane sources continuous to be of great importance in this field of research with possible future policy implications. This study reflects important incremental progress and the fact that it emphasis the value of double isotope analysis make it very relevant beyond the immediate study region. The quality and scope of the paper is, therefore, fully suitable for publication in Atmospheric Chemistry and Physics. However, there are two general issues and a few very minor comments that should be addressed before publication.

> Author's response:
>
> We thank the reviewer for this constructive feedback on the manuscript, and the positive comment about this research being important. Below we address the concerns raised, and we have followed the suggestions where we feel that they improve the quality of the manuscript. All authors thank the reviewer for reading the manuscript carefully, and for making insightful recommendations.

- Representativeness of results:

Without further information on the type of landfill and WWTP for example it seems impossible to judge if the found isotopic signatures can be used for other such facilities in the regions. The same problem arises for the piggery and especially the abattoirs where the source mix/methane producing process seems unclear. Are the isotopic signatures presented here representative for each class of facility in the region or will future studies have to be conducted to characterize each piggery and abattoir seen in Figure 1? This should be discussed in more detail in the conclusion section.

Author's response:

We acknowledge the importance and challenges with quantifying how representative the presented isotopic signatures are. Collating statistically robust data sets for the isotopic signature of all primary CH_4 sources is a time-consuming and costly endeavour. For this study we collected and analysed over 160 bag samples. Some of the data presented in the manuscript are the first and only data we have for that source under Australian conditions (e.g., abattoirs and piggeries).

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 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 […]"

- Calculation of uncertainties:

The uncertainties reported seem to only rely on the uncertainty of the Miller-Tans fit. However, for some plumes e.g. the river seep (Figure A2) only 4 data points are available and any sub-sample of 3 of those data points could yield different results. As the isotopic signatures rely on very few data points per site (some on only 3 data points) it seems reasonable to use leave-one-out-validation to check if the Miller-Tans fit uncertainty is reasonable. For some sites the current uncertainties could just reflect the lower bound of the true uncertainty, which is not highlighted in the conclusion section.

Author's response:

We acknowledge that the small sample size is an issue with some of the bag sets collected to determine the isotopic signature of individual sources. "Leave-one-out" or "Bootstrapping" is not appropriate for such small data sets, because there are too few points to establish the population distribution statistics from the limited number of permutations. We used Bayesian regression, because it is widely considered as one of the more robust measures for characterising parameter uncertainty, via the credible interval (analogous to the confidence interval in ordinary least squares regression). Please refer to Beckman and Cook (1983) and McNeish (2016).

Beckman, R. J. and Cook, R. D.: Outlier … … …. s, Technometrics, 25(2), 119–149, https://doi.org/10.1080/00401706.1983.10487840, 1983.

McNeish, D.: On Using Bayesian Methods to Address Small Sample Problems, Struct. Equ. Model. A Multidiscip. J., 23(5), 750–773, https://doi.org/10.1080/10705511.2016.1186549, 2016.

The Bayesian Regression workflow and determination of the credible interval is comprehensively discussed on the Wolfram web pages:

https://blog.wolfram.com/2019/08/22/embracing-uncertainty-better-model-selection-with-bayesian-linear-regression/.

There is also a good introductory discussion on the difference between Bayesian and Ordinary Least Squares regression by Koehrsen (2018):

https://towardsdatascience.com/introduction-to-bayesian-linear-regression-e66e60791ea7

We have replaced the term "uncertainty (ies)" with "credible interval" to better convey the use of Bayesian statistics, not frequentist statistics.

Specific and technical comments:

L5: If appropriate, consider spelling out the name of the University of New South Wales Sydney here.

Author's response:

UNSW Sydney is the official brand of our institution. We have made the following change:

L5: "[…] The University of New South Wales Sydney (UNSW Sydney) […]"

L17: Why is this limited to 'warm and hot climate regions''? Even in temperate and colder climates, nighttime GHG levels are known to be enhanced compared to afternoon values due to less vertical mixing in a lower PBL.

Author's response:

The authors agree; therefore, the sentence has been rephrased to the following:

L17: "[…] We also highlight the benefits of sampling at nighttime ~~in warm to hot climate regions~~ […]"

L19: Were all 17 plumes analysed for δD_{CH4}? Only 14 sites are given in Figure 3 (and the tables) what happened to the δD_{CH4} data from the other sites (e.g. the Chinchilla landfill)?

Authors' response:

We acknowledge that this sentence about the δD_{CH4} analyses was not clear. Unfortunately, due to a limited budget, only a selected set of samples was analysed for δD_{CH4}. To clarify, we have added "from 13 sources" in L273:

L273: "[…] A portion of the samples (from 13 plumes) was further analysed in the Institute for Marine and Atmospheric research"

L40: Nisbet et al. 2020 is a great reference here, but IPCC AR5 (you cite Myrhe et al. 2013 later on) and others (e.g. Ganesan et al. 2019) could be/should be mentioned as well.

https://agupubs.onlinelibrary.wiley.com/doi/full/10.1029/2018GB006065

Authors' response:

We thank the reviewer for this suggestion, and we have added these most useful references (in addition to corrections implemented in RC#1 – Comment P2 L40): L40 now reads "[…] to anthropogenic industrial and agricultural activities (e.g. Ganesan et al., 2019; IPCC, 2014; Nisbet et al., 2020)."

The following references are added to the updated manuscript:

Ganesan, A. L., Schwietzke, S., Poulter, B., Arnold, T., Lan, X., Rigby, M., Vogel, F. R., van der Werf, G. R., Janssens-Maenhout, G., Boesch, H., Pandey, S., Manning, A. J., Jackson, R. B., Nisbet, E. G. and Manning, M. R.: Advancing Scientific Understanding of the Global Methane Budget in Support of the Paris Agreement, Global Biogeochem. Cycles, 33(12), 1475–1512, https://doi.org/10.1029/2018GB006065, 2019.

Pachauri, R. K. , Allen, M. R. , Barros, V. R. , Broome, J. , Cramer, W. , Christ, R. , Church, J. A. , Clarke, L. , Dahe, Q. , Dasgupta, P. , Dubash, N. K. , Edenhofer, O. , Elgizouli, I. , Field, C. B. , Forster, P. , Friedlingstein, P. , Fuglestvedt, J. , Gomez-Echeverri, L. , Hallegatte, S. , Hegerl, G. , Howden, M. , Jiang, K. , Jimenez Cisneroz, B. , Kattsov, V. , Lee, H. , Mach, K. J. , Marotzke, J. , Mastrandrea, M. D. , Meyer, L. , Minx, J. , Mulugetta, Y. , O'Brien, K. , Oppenheimer, M. , Pereira, J. J. , Pichs-Madruga, R. , Plattner, G. K. , Pörtner, H. O. , Power, S. B. , Preston, B. , Ravindranath, N. H. , Reisinger, A. , Riahi, K. , Rusticucci, M. , Scholes, R. , Seyboth, K. , Sokona, Y. , Stavins, R. , Stocker, T. F. , Tschakert, P. , van Vuuren, D. and van Ypserle, J. P., Pachauri R.K. and Meyer L.A. (Eds.): Climate Change 2014: Synthesis Report. Contribution of Working Groups I, II and III to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change, IPCC, Geneva, Switzerland, 151 pp., https://epic.awi.de/id/eprint/37530/, 2014.

L41: Suggest rephrasing to "not **always** possible" or "not **easily** possible" as it is indeed possible to identify sources from atmospheric mole fraction measurements when sources are **not** juxtaposed and isolated enough and/or when suitable calibrated atmospheric modelling can be performed.

Authors' response:

The authors thank the reviewer for this suggestion. We have edited L41 to read:

L41: "in the atmosphere it is not always possible to isolate the source of the emission, especially if many sources are juxtaposed […]"

L152 (and following): Why is 'coal seam gas' not abbreviated as CSG here? Suggest to consistently use CSG throughout the manuscript. Possible exception at beginning of new sections if readers 'jump' directly to the conclusions it might be useful to reintroduce CSG.

Authors' response:

Agreed and revised throughout the text. Please also refer to our response to RC#1 – Technical Comments regarding the consistent use of the abbreviation CSG.

L157: Further information on the power stations seems necessary, how many are gasfired and how many are coal-fired? Also, they account for 4.7% of GHG emissions from the electricity sector, but is this mostly due to their CO_2 emissions or do they report significant loss rates for CH_4 as well?

Authors' response:

We thank the Referee for the comment. We've added the number of gas- and coal-fired power stations. There is now a comprehensive inventory for the region of study, including details on how the CH_4 emissions were estimated, in Neininger et al. (under review). The estimated CH_4 emissions from the power plants is 0.15 % of the regional CH_4 emissions. L157 has been edited to read:

L157: "[…] In the study area, seven power stations (5 CSG–fired and 2 coal–fired) are operational in the area of study and together they account for 0.15 % of the CH_4 emissions for the south-east portion of the Surat Basin CSG fields (Neininger et al., in review) […]"

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, 2021.

L174: Correct to "fa**r**ming"

Authors' response: Agreed and revised to the following:

L174: "[…] Most cattle in the region are in the surrounding dryland farming districts […]"

L199: Here the authors nicely outline which factors determine landfill emissions, but none of the suggested parameters controlling landfill CH_4 production is reported for the Chinchilla landfill.

Authors' response:

Little or no information is in the public domain for small country town landfills in Australia. Chinchilla has a population of 6612 people at the last census (https://quickstats.censusdata.abs.gov.au/census_services/getproduct/census/2016/quickstat/SSC30606).

We added the following sentence at L202:

L202: "[…] The landfill is typical of many small-town landfills in the region, and when operational it accepted mixed dry and solid organic domestic waste, commercial and industrial waste. These landfills have a simple design and typically have a clay lining and soil cover. A full listing of the landfills in the study area and the materials deposited within each are listed in Western Downs Regional Council (2021a)."

The following reference has been added:

Western Downs Regional Council: Waste Facilities & Disposal Fees, https://www.wdrc.qld.gov.au/living-here/environment-and-health/waste-disposal/waste-facilities/, last access: 29 April, 2021a.

L201: The amount of (organic) waste deposited at this landfill site would seem a critical parameter to add here (its disposal area might be of secondary importance).

Authors' response:

We agree with the Referee that knowing the amount of (organic) waste deposited at this landfill site would be beneficial. However, due to limited public information, no specific data about the proportion of organic versus other waste could be found. Please refer to the response to Comment L199.

L205: What kind of waste treatment is used at the Miles WWTP, e.g. are sludge digesters used?

Authors' response:

We thank the Referee for highlighting this. We have added more details as follows:

L205: "[…] In 2019 we sampled the plume immediately downwind of the Miles wastewater treatment plant. There, the sludge was treated in digestion tanks under anaerobic conditions. The liquid from the tanks was then transferred to the aerobic lagoons for further purifying (Western Downs Regional Council, 2021b)."

We added the following reference:

Western Downs Regional Council: Regional Sewerage Networks, https://www.wdrc.qld.gov.au/living-here/engineering-services/utility-services/wastewater-and-sewerage/regional-sewerage-networks/#miles-sewerage, 29 April, 2021b.

L220-L230: Suggestion to cite appropriate peer-reviewed studies on instrument performance rather than only manufacturer specifications. Previous studies have investigated the performance of G2201i and UGGA instruments e.g.

https://www.sciencedirect.com/science/article/pii/S0956053X17309698

https://www.gov.uk/government/uploads/system/uploads/attachment_data/file/331683/S C130034_Report.pdf

https://amt.copernicus.org/articles/8/4539/2015/

https://amt.copernicus.org/articles/10/2077/2017/

Authors' response:

We agree that further details on the performance of the analysers should be added. It needs to be noted that only the Picarro G2201-i CRDS CH_4 mole fraction data from mobile surveys were used in this manuscript. All Keeling and Miller–Tans plot analyses used the results from the higher precision RHUL Picarro G1301 CRDS, GC-IRMS and IMAU CF-IRMS systems as detailed in the manuscript. We modified the following text and provided in-field performance data in the Appendix (please refer to our response to RC#1 – General Comment 3):

L219: "records the CH_4 mole fraction ~~data~~ every second in parts per million (ppm). The manufacturer's ~~with a~~ stated precision is ~~(~~1 standard deviation~~)~~ of <2 parts per billion (ppb) and a measurement range of 0 to 100 ppm. These analysers were further characterised by Allen et al. (2019). In-field calibration using southern-ocean air supplied by CSIRO is discussed further below. The air inlet […]"

L230: "[…] of < 1.15 ‰ at 10 ppm. Previous studies have also characterised the Picarro G2201-i performance (e.g., Assan et al., 2017; Rella et al., 2015) […]"

The following references has been added:

Allen, G., Hollingsworth, P., Kabbabe, K., Pitt, J. R., Mead, M. I., Illingworth, S., Roberts, G., Bourn, M., Shallcross, D. E. and Percival, C. J.: The development and trial of an unmanned aerial system for the measurement of methane flux from landfill and greenhouse gas emission hotspots, Waste Manag., 87, 883–892, https://doi.org/10.1016/j.wasman.2017.12.024, 2019.

Assan, S., Baudic, A., Guemri, A., Ciais, P., Gros, V. and Vogel, F. R.: Characterization of interferences to in situ observations of $\delta^{13}CH_4$ and C_2H_6 when using a cavity ring-down spectrometer at industrial sites, Atmos. Meas. Tech., 10(6), 2077–2091, https://doi.org/10.5194/amt-10-2077-2017, 2017.

Rella, C. W., Hoffnagle, J., He, Y. and Tajima, S.: Local- and regional-scale measurements of CH_4, $\delta^{13}CH_4$, and C_2H_6 in the Uintah Basin using a mobile stable isotope analyzer, Atmos. Meas. Tech., 8(10), 4539–4559, https://doi.org/10.5194/amt-8-4539-2015, 2015.

L224: The cited precision of 8cm is likely only for static measurements. Typically, the limiting factor for the resolution on mobile platforms is the GPS frequency. Was the 10Hz or the optional 20Hz version of the A326 used here?

Authors' response:

We acknowledge that the precision of the GPS is for the static measurement. We have modified the following text:

L221 – L223: "[…] A Hemisphere GPS (Model A326, Hemisphere GNSS Inc., USA) was also mounted on the roof, which measures the static geolocation to within 8 cm (2 standard deviations, GNSS 2017). The air inlet tube was 2.5 m long; this results in a lag between the GPS recorded time stamp and the analyser time stamp. Using standard air this was determined to be 7 s. It was not the goal of the project to do detailed plume analyses. Driving speed was not independently continuously measured, and only a lag time correction was made. As a result, the surveys were not precisely positioned. When a major plume was traversed, we returned to the centreline of the plume and remained stationary to georeference the plumes shown in Fig. 2. The car was stationary for up to half an hour while the air samples were collected. In Fig. 2 the plume positions are accurately located, but away from the plumes the survey results are only approximate to within the order of tens of meters."

L230: see L224

Authors' response: Please refer to our response to Comment L224.

L319: Are those uncertainties only based on the uncertainty of the fit or was a bootstrapping method used as well to check that individual data points do not overly bias the slope? Was any data selection applied, i.e. only accepting slopes of fits with an R^2 above a threshold value?

Authors' response:

Bayesian regression is a robust regression method – it was selected because it reduced the influence of outliers on the derived statistics. The uncertainty, or better-termed credible interval, is not determined from a single line of best fit; rather it is determined from the posterior distribution of the parameters.

L325 – Figure 2: The three reference levels of CH_4 (3, 2 and 1.8ppm) are rather confusing and make the figure more difficult to follow. As all major peaks are labelled with their concentration this seems unnecessary (or maybe just have one reference level). The grey ribbon is hardly visible with blue and green levels on the figure.

Authors' response:

As recommended by the reviewer we have removed the 3 and 2 ppm reference level lines but left the reference 1.8 ppm line in the updated Fig. 2.

L330 – Table 1: Please add the range or maximum CH_4 mole fraction for each plume, additionally the Pearson's R or R^2 of the Miller-Tans fit might be informative. Furthermore, it seems important to highlight if the samples were part of a daytime or nighttime survey.

Authors' response:

R and R^2 are only suitable measures for ordinary least squares regression (a frequentist approach). There is no universally accepted Bayesian equivalent of R or R^2. Please refer to Gelman et al. (2019) for further details on this topic. The goal in using Bayesian regression is to robustly determine the credible interval for the isotopic signature. It is not to assess the deviation of points from the linear regression model, which is the information provided by R and R^2.

We have added to Table 2 the highest excess over background for the samples used to calculate the source signature.

L339 – Could ground migration/stray natural gas migration be important here? If yes, this means emissions can be significantly displaced from the actual leaking infrastructure.

Authors' response:

We believe that the ground migration/stray natural gas migration is not of concern here. The CH_4 enhancement measured in the study was closely related to the source (infrastructure) we identified. At all CSG locations, distinct plumes were discernible, and we traced each plume close to each facility.

L387 – Figure 4: The current figure makes it difficult to compare literature sources and this study. A two-panel figure with the same size and same X&Y scaling could make it easier. Alternatively, adding PM, SM and T areas to the main part of Figure 4 would achieve the same.

Authors' response:

We thank the reviewer for this feedback and have adopted the suggestion. We have changed Fig. 4 in the manuscript.

L395 – The abbreviation ROM seems not to be used elsewhere in the manuscript.

Authors' response:

We thank the Referee for highlighting this oversight, and we have made the following change in the sentence:

L395: "with permission to extract up to 2.8 million tonnes per annum (Mtpa) of run-of-mine ~~(ROM)~~ coal (Yancoal, 2018) […]"

L440 – Why are no δD_{CH4} values reported for abattoir A?

Authors' response:

Unfortunately, due to a limited budget, only a selected set of samples was analysed for δD_{CH4}. Please refer to our response for Comment L19 for additional discussion on this point.

L469 – Please state more clearly what your theory is about the source of the CH_4 from abattoir A and B. There is a discussion of different options which are likely not the source and eventually, I think, you are suggesting that there is a biogas generator on site or a waste lagoon that is causing the emissions?

Also, if one of the abattoirs actually has an integrated feedlot and we cannot be sure what the source is, are the values found for this abattoir applicable to other abattoirs?

Authors' response:

There are only two large meat processing facilities in the region – Beef City and Oakey Beef Exports. Throughout the text when referring to these meatworks we now write abattoirs (meat works and processing) to separate them from licensed abattoir locations, which may be a small facility on a private property (such details are not provided with the government records). In Fig. 1, we now show them separately as "export abattoirs (meat works and processing)" and "licensed abattoirs".

Both abattoirs are multi-purpose facilities, consisting of animal management areas, slaughter facilities with venting stacks, meat and other processing as stated in L446 to L448. Due to limited site access, we were unable to closely investigate individual sources. We therefore highlighted in L450 that the plume we sampled was most likely from mixed sources (a meat works facility value, not an isolated source value).

L523 – What kind of aerobic and/or anaerobic treatment is implemented at the Miles wastewater treatment plant? A simple description in section 2. might be helpful to understand why it is more similar to some WWTPs from previous studies.

Authors' response: Please refer to our response to Comment L205.

L530: Was the consumer grade natural gas used in the city measured or were samples from wood stoves taken? If not, those seem important sources to add in future studies.

Authors' response:

We have deleted the contents about mixed urban emissions. Please refer to our response for RC#1 – Comment P18 L446. We did this for two reasons. At the regional level we have now determined that the CH_4 emissions from the towns is only a minor source of CH_4 (Neininger et al. (under review). Also, as these urban results were a highly blended signature, and the focus of the paper is on individual sources or facilities, we have removed all discussions on the urban emissions and blended isotopic signature from the manuscript. Ideally each source in a town should be characterised, but that was beyond the scope of this project.

L590-L600: Seems to be a summary, rather than contain conclusions. Other parts of this section also seem to repeat previous results. Therefore, renaming the section to "Summary and conclusion" might be appropriate.

Authors' response:

We agree with the Referee; the section has been renamed as follows:

L592: "4 Summary"

L607: Are the samples for piggeries and abattoirs representative of other facilities of the same type in Queensland or even Australia (see general comments).

Authors' response:

The majority of piggeries in Australia have a common design, to maximise the health and safety of the pigs, and to reduce the environmental impacts. For example, refer to:

http://australianpork.com.au/wp-content/uploads/2018/08/NEGIP_2018_web.pdf

L625 – Suggest to add Pearson's R or R^2 for each Miller-Tans fit in Figures A1, A2. A3, A4 and A5.

Authors' response:

As discussed already, R and R^2 are frequentist statistical measures for ordinary least squares (OLS) regression. There is no direct equivalent measure for Bayesian regression. We did not use ordinary least squares regression, because it is well established that when there is error in both the X and the Y variables it is not an appropriate method to use.

References

Beckman, R. J. and Cook, R. D.: Outlier … … …. s, Technometrics, 25(2), 119–149, https://doi.org/10.1080/00401706.1983.10487840, 1983.

Gelman, A., Goodrich, B., Gabry, J. and Vehtari, A.: R-squared for Bayesian Regression Models, Am. Stat., 73(3), 307–309, https://doi.org/10.1080/00031305.2018.1549100, 2019.

McNeish, D.: On Using Bayesian Methods to Address Small Sample Problems, Struct. Equ. Model. A Multidiscip. J., 23(5), 750–773, https://doi.org/10.1080/10705511.2016.1186549, 2016.