Author's Response to Referee#2 Comments on: "Six years of continuous carbon isotope composition measurements of methane in Heidelberg (Germany) – a study of source contributions and comparison to emission inventories"

We thank the Referee#2 for the careful reading and appreciate the referee's suggestions. These helped us improve the manuscript.

General Comments:

[Referee#2] In this paper, Hoheisel et Schmidt describe new continuous CH4 and δ(13C,CH4) measurements retrieved between 2014 and 2020 In Heidelberg (Germany). After introducing the experimental setup, they analyze the temporal variability of this data and apply the Miller-Tans method to derive estimates of the mean isotopic signature that could cause these variations. These determined estimates are then compared to bottom-up estimates using two different inventories.
Overall, the paper is well presented and well written. The structure is clear and it is easy to understand where the authors are leading us. Also, the scientific questions addressed in this study are well within the scope of ACP and the analysis conducted to answer these questions is detailed, elaborate and tackles very interesting points, both for experimentalists and atmospheric modelers.
Last but not least, this new continuous data is invaluable to better investigate methane sources and will likely be utilized in the future by the rest of the atmospheric community. Most of my comments only call for additional clarity in the methodology and the presentation of results. Also, a few additional details in the methodology and in the results would be beneficial both for the reproducibility of the study and the comprehensiveness of the analysis. However, these comments are very minor and I can already recommend this paper for a publication in the journal ACP.

Specific comments:

[Referee#2] Line 1: I recommend not using the abbreviation $\delta(^{13}CH_4)$ in the abstract. Use $\delta(^{13}C,CH_4)$.

[Hoheisel and Schmidt] Yes, we changed $\delta(^{13}CH_4)$ to $\delta(^{13}C,CH_4)$ in the abstract.

[Referee#2] Line 2: You write that it is a 6-year time-series, since 2014. It may give the reader the impression that the measurements stopped in 2020. I suggest a small revision: "Between 2014 and 2020, the time series shows an increasing trend of (6.8 ± 0.3) nmolmol−1 a−1 for the CH4 mole fraction."

[Hoheisel and Schmidt] Thank you for the helpful suggestion. This will make the text more comprehensible. We changed the sentence in the revised manuscript.

[Referee#2] Line 6: At present, it seems you are using $\delta(^{13}C,CH_4)$ (abbreviated as $\delta(^{13}CH_4)$) for atmospheric isotopic composition and $\delta^{13}C$ (also an abbreviation of $\delta(^{13}C,CH_4)$) for isotopic signature. In my opinion, it's okay to keep it that way but you should not use the abbreviations in the abstract and also introduce the abbreviation $\delta^{13}C$ in the main text.
Line 166: You should very briefly introduce the abbreviation δ13C the same way you introduced it for $\delta(^{13}CH_4)$ for the atmospheric isotopic composition.

[Hoheisel and Schmidt] Thank you for pointing this out. To avoid confusion, we have replaced the term '$\delta^{13}C$ isotopic source signature' with 'isotopic carbon source signature'.

[Referee#2] Line 9: Sentence not clear. As far as I understand, the mean estimated δ(^{13}C,CH_4) source isotopic signature exhibits a seasonal variation, with a peak-to-peak variation -6.2 ‰. If it is the case, you should reformulate. I suggest replacing the sentence "This annual cycle in ^{13}C-CH_4 sources…", with "This annual cycle in the mean source isotopic signature source, with a peak-to-peak amplitude of −6.2‰, can only be partially explained by seasonal variations in the ^{13}C-enriched emissions from heating."

[Hoheisel and Schmidt] Yes, you understand it right. We changed the sentence in the revised manuscript according to your suggestion.

[Referee#2] Line 25: After this sentence, you should introduce the isotopic scale δ(^{13}C,CH_4) with a formula. Because after that you provide typical source signature values for different source categories (e.g. −55‰ to −70‰), but the reader does not know what scale you are referring to. You could also be talking about ^{14}C rather than ^{13}C.
Line 99: Would be worth mentioning the value you are using for the reference ^{13}C/^{12}C ratio because there is sometimes confusion between PDB and VPDB values.

[Hoheisel and Schmidt] As suggested, we included an introduction to the δ –notation and the VPDB values in the revised manuscript:
"The isotopic composition of methane δ(^{13}C,CH_4), hereafter abbreviated as δ($^{13}CH_4$), is described with the δ –notation, using the isotopic ratio R, and is typically given in ‰. The international reference standard for δ($^{13}CH_4$) is the Vienna Pee Dee Belemnite (VPDB; 0.0111802±0.0000028, Werner and Brand, 2001).
$\delta = R_{sample}/R_{standard} - 1$; $R = {}^{13}CH_4/{}^{12}CH_4$"

[Referee#2] Line 30: Give the recent references for these values also here (e.g., Sherwood et al. 2017; 2021; Menoud et al., 2022). Also, the thermogenic range you provide appears slightly inconsistent (too small and too enriched) when compared to the information presented in these references.

[Hoheisel and Schmidt] This paragraph in the introduction is intended to give an overview of the different CH_4 sources and their typical isotopic source signatures. As indicated in the manuscript, we have taken the typical isotopic source signatures from the IPCC AR5 WG1 report from 2013. Individual measurements and especially more recent measurements may of course deviate from these typical values. To avoid any misunderstandings, we have changed the paragraph and added a sentence that discusses the more recent measurement results.
"*CH_4 is emitted from anthropogenic and natural sources, which are grouped in three different categories according to the production processes. Biogenic CH_4 is produced under anaerobic conditions due to degradation of organic matter (typically -70‰ to -55‰; IPCC, 2013). Biogenic CH_4 sources are wetlands, ruminants, landfills and wastewater treatment plants. Thermogenic CH_4, like that in natural gas, is formed on geological time scales out of organic matter and is less depleted than biogenic CH_4 (typically -45‰ to -25‰; IPCC, 2013). Pyrogenic CH_4 is formed during the incomplete combustion of organic matter, such as biomass burning, and is more enriched (typically -25‰ to -13‰; IPCC, 2013)* compared to biogenic and thermogenic CH_4. *Studies by Sherwood et al. (2017; 2021) and Menoud et al. (2022) show that the δ^{13}C-CH_4 values of the different source categories are not always as distinct as indicated above. They give much larger ranges of δ^{13}C-CH_4 values for the different source categories, which also overlap as a result. Especially for fossil but also for biogenic sources large regional differences occur."*

[Referee#2] Line 59: “To our knowledge, our time series is the longest in situ δ($^{13}CH_4$) record, with high temporal resolution, reported to date.”. You mean the longest for Heidelberg or the longest ever in the world?

[Hoheisel and Schmidt] We mean, that to our knowledge our time series is the longest published time series measured with a high temporal resolution instruments in the world.

[Referee#2] Line 64: A continuous six-year time series between when and when?

[Hoheisel and Schmidt] We included the measurement years in the revised manuscript.

[Referee#2] Line 119: I think two significant figures is not enough for δ($^{13}CH_4$). I would recommend three, as you do in the rest of the paper. If we look at the bulk, I mostly see values between -49.0‰ and -47.5‰. If you also want to include extreme values, then it is approximately -49.5‰ to -47.2‰

[Hoheisel and Schmidt] As recommended, we changed the number of significant figures to three for δ($^{13}CH_4$) in the revised manuscript:
“*The corresponding isotopic composition δ($^{13}CH_4$) ranges from -49.3‰ to -47.3‰.*“

[Referee#2] Line 123: Please plot the trend on Figure 3. I think if you increase the size of the figure and increase the transparency of the 1day averages, then it won’t decrease the overall clarity.

[Hoheisel and Schmidt] As suggested, we have added the trend in Figure 3 of the revised manuscript.

[Referee#2] Line 127: Less enriched compared to what? To the mean? Overall, I think some confusion can arise from the fact that you use the mean over the full time series as the center of your annual cycle, rather than using zero. Line 128 and 129 suggest that the values are always -48.3‰ in early autumn and -47.9‰ in spring, while these values have an interannual variability, due to the trend and the variations in the seasonal cycle. It’s okay to keep it that way but you should comment on that.

[Hoheisel and Schmidt] Thank you for your comment. We have chosen to add the mean values when presenting the mean annual cycles, as in our opinion this enables a more intuitive understanding of the annual cycles. However, we agree with you that stating the maximum and minimum values in the text, in the way we have done it, can lead to confusion and misunderstandings. We have therefore changed the sentence in the revised manuscript:
“The annual cycle in atmospheric δ($^{13}CH_4$) has a mean amplitude of 0.4‰. In early autumn (September to October) the δ($^{13}CH_4$) values are more depleted than the values in spring (April to May).”

[Referee#2] Line 139: After the analysis in Section 3.3, can you think of a reasonable explanation?

[Hoheisel and Schmidt] The stronger influence of biogenic emissions in summer could lead to patterns in the measured δ($^{13}CH_4$) values in Heidelberg, such as the lower values in fall or the greater amplitude in the diurnal cycle in summer. However, other factors such as the OH sink also play a role in the measured atmospheric δ($^{13}CH_4$) values, so we do not want to over interpret the influence on the measured δ($^{13}CH_4$) values.

[Referee#2] Line 146: Could you provide the details of the Mace Head Observatory (altitude, longitude, latitude)? Also, please explain why Mace Head can be considered as a "background" station.

[Hoheisel and Schmidt] We included more details about the Mace Head Observatory in the revised manuscript: "*The Mace Head Observatory (53°19'36"N, 9°54'16"E, 8.4m a.s.l.) is located on the west-coast of Ireland and measures the maritime background mole fraction when air is coming from the ocean.*"
We are aware that Mace Head is not optimal as a background station for Heidelberg. However, since this is the only background station west of Heidelberg with a long published $\delta^{13}C\text{-}CH_4$ record, we have decided to use the data from Mace Head to characterise and compare the Heidelberg measurements of today (2014-2020) and the 1990s.

[Referee#2] Line 156: In this paragraph, you use both "emissions in Heidelberg" and "emissions in the catchment area of Heidelberg". Is it supposed to mean the same thing (I suppose so)? Or did Levin et al. (2011, 2021) only analyze emissions in the city of Heidelberg (without the surroundings)?

[Hoheisel and Schmidt] Yes, we meant the same with the terms "emissions in Heidelberg" and "emissions in the catchment area of Heidelberg". Thank you for pointing out this inaccuracy. We corrected this in the revised manuscript.

[Referee#2] Line 182: If you want to make a comparison between the Miller-Tans method and the Keeling plot, which is a good idea, you should briefly introduce the Keeling plot method as well.

[Hoheisel and Schmidt] Thank you for pointing this out. We have changed large parts of subsection 3.3.1 on the Miller-Tans and Keeling plot methods in the revised manuscript to clarify the methods we use based on Referee#1's comments. We also included a short introduction to the Keeling plot and the Miller-Tans methods.

[Referee#2] Line 187 and line 200: Which CH_4 range? Apologies for being confused here. You discard every data point where the difference between C_{bg} and C_{obs} is below 100 nmol mol-1? If it is the case, for the night data set, do you discard the full night if one of the data points does not satisfy this criteria?

[Hoheisel and Schmidt] Thank you for this helpful comment. We have changed the paragraph in the revised manuscript to clarify our selection criteria. With 'CH_4 range', we did not mean the difference between C_{bg} and C_{obs}, but the difference between the minimum and maximum observed CH_4 values (C_{obs}).
"*The uncertainty of the source signature determined with the Keeling plot method and the York fit strongly depends on the precision of the analyser and the peak height of CH_4 (Hoheisel et al., 2019). To achieve accurate results for the mean isotopic carbon source signatures, we apply two criteria to our data: the CH_4 range of the dataset, to which the Keeling plot is applied, has to be larger than 100 nmol mol^{-1} and the fit error on the slope of the regression line has to be smaller than 2.5‰.*"

[Referee#2] Line 193: Please, reformulate. What can be assumed? That it is constant?

[Hoheisel and Schmidt] We reformulated the sentence in the revised manuscript:
"*However, for such large time intervals of one month, the assumption of a constant background, which is used in the Keeling plot method, is not correct and could lead to errors in the determined isotopic source signatures. This problem is less prominent for the night-time and moving Keeling plot approach, as in these approaches shorter time periods of a few hours are used.*"

[Referee#2] Line 213: What do you mean by ‘directly adjacent in time’? What amount of time do you consider to be ‘adjacent in time’? And what percentage of the 18% are during night time?
In general, I do not understand how long an “event” is. Therefore, it is difficult to confirm that a night time increase can influence the event detected by the Miller-Tans approach. It would be nice to show somewhere the typical length of an event. Do these events happen mostly during the night? As far as I understand, you can access this information with your methodology.

[Hoheisel and Schmidt] 53% of the 18% mean isotopic source signatures of the moving Miller-Tans/Keeling plot approach which met our criteria are during the night.
Based on your comments and the ones from Referee#1, we had a closer look at the automatically generated events and decided not to split the moving Miller-Tans/Keeling plot results into individual events any more. Instead, we will examine the hourly and daily averages of the results of the moving Keeling plot. We changed this in the revised manuscript accordingly.

[Referee#2] Line 222: Here and throughout the text, you often use “more/less depleted” or “more/less enriched”. Usually, a value is depleted/enriched compared to a point of comparison, which is often the atmospheric value (around -48.07‰ in your case), as you state it very clearly in the following sentence. For instance, in this situation, I would use “more depleted” rather than “less enriched” because the source signatures for the moving Miller-Tans and night time approaches are already depleted compared to the atmospheric composition. Therefore, the third one is even more depleted.
Line 292 and onwards: Again “more depleted” compared to what?

[Hoheisel and Schmidt] Thank you for this important comment. Unfortunately, we missed this inaccuracy while writing the manuscript. We went through the entire document again and tried to formulate the comparison of isotopic source signatures and $\delta^{13}C\text{-}CH_4$ more precisely.

[Referee#2] Line 224: It seems that you are suggesting there is a causality between the fact that the estimated source isotopic signature is more depleted than the atmospheric composition and the fact that biogenic sources play a dominant role. I do not think it is true. You can suggest biogenic sources are dominant because the estimated source signature is low and close to what could be expected if biogenic sources (typically between -55‰ and -70‰) were dominant. Or to the contrary, it would be too low compared to a situation where only pyrogenic and thermogenic were dominant (although some thermogenic sources can have a source isotopic signature as low as -60‰, see Sherwood et al., 2017).

[Hoheisel and Schmidt] Thank you again for pointing out inaccuracies and imprecision in our text. We corrected the sentence according to your suggestions in the revised manuscript:
“Since the determined mean isotopic source signature is low and close to what could be expected if biogenic sources (typically between -55‰ and -70‰) were dominant, a strong influence from biogenic CH_4 sources, such as waste management and agriculture, in the catchment area of Heidelberg can be assumed.”

[Referee#2] Line 271: Please reformulate. Do you mean both explanations are plausible? Is it exclusive? The too at the end is a bit misleading.

[Hoheisel and Schmidt] Yes, both explanations are plausible. We changed the sentence in the revised manuscript.

[Referee#2] Line 280: You suggest two explanations but as far as I understand, both explanations are closely linked. Small pollution events of the first explanation can be the ones from distant sources from the second explanation. If it is correct, maybe you could mention it at the end of the paragraph.

[Hoheisel and Schmidt] Thank you for this constructive comment. We agree that the paragraph is not clear enough and have reworked it slightly in the revised manuscript.

[Referee#2] Line 303: "The monthly values vary on average between 0.1‰ and 0.8‰". What does the percentage represent?

[Hoheisel and Schmidt] Thank you for your comment. We noticed, that this sentence does not clearly describe the deviations which occur, when using different selection criteria. The values 0.1‰ and 0.8‰ represent differences in the monthly mean isotopic source signatures calculated using different selection criteria. We changed the sentence in the revised manucript:
"The monthly mean isotopic source signatures calculated with different selection criteria show differences between 0.1‰ and 0.8‰, with standard deviations between 1‰ and 3‰."

[Referee#2] Line 319: Give the exact location of the station.

[Hoheisel and Schmidt] We included the location of the Schauinsland station in the revised manuscript: 47°54'50'' N, 7°54'28'' E, 1205m a.s.l.

[Referee#2] Line 340: You have only one subsection 3.4.1 under section 3.4. Shouldn't section 3.5 and 3.6 be subsections of sections 3.4? Or at least section 3.5?

[Hoheisel and Schmidt] Yes you are right, thank you very much. Section 3.5 and 3.6 should be subsections of 3.4. We changed it in the revised manuscript.

[Referee#2] Line 354: Why does it "seem" to decrease? If you are not confident, where does this number 7%, without any uncertainty, come from?

[Hoheisel and Schmidt] Thanks. We have corrected the sentence in the revised manuscript.

[Referee#2] Line 389: It is not clear what you needed.

[Hoheisel and Schmidt] During the development process of the paper, the paragraph in line 389 changed several times, so that in the end it unfortunately became misleading and imprecise. We only wanted to express that, despite extensive literature research, we have not found a study that has determined and reported the $\delta^{13}C\text{-}CH_4$ isotope signature of waste incineration. We have changed the sentence in the revised manuscript.

Technical comments:

[Referee#2] Figures: Although they have a good resolution, I would have preferred the figures to be larger, i.e. fitting the width of the page.

[Hoheisel and Schmidt] This is a good point. The reason we chose this width is to comply with the guidelines of the journal. Hence, if the editor agrees I would be happy to enlarge the width.

[Referee#2] Figure 1: In the caption, map data on from → map data from

[Hoheisel and Schmidt] We corrected it in the revised manuscript.

[Referee#2] Figure 3: There is a problem with the x-axis ticks of the top-right panel. Please, make it similar to the bottom-right panel. Also, please add in the caption a note saying that the y-axis ranges are not the same for the left and right panels.

[Hoheisel and Schmidt] Many thanks for the hint. We have corrected the figure and added a sentence regarding the y-axis ranges in the revised manuscript.

[Referee#2] Line 67: to CH_4 total emissions.

[Hoheisel and Schmidt] We corrected it in the revised manuscript.

[Referee#2] Line 152: Replace with “This was different” or “this is different for the 1990s”

[Hoheisel and Schmidt] We corrected it in the revised manuscript.

[Referee#2] Line 180: Put these subscripts in the same format as in the equation.

[Hoheisel and Schmidt] We changed it in the revised manuscript.

[Referee#2] Line 214: Do you mean 2014 instead of 2011?

[Hoheisel and Schmidt] Yes exactly, we meant 2014. We corrected it in the revised manuscript.

[Referee#2] Line 266: Although → However

[Hoheisel and Schmidt] We changed it in the revised manuscript.

[Referee#2] Line 274: less enriched → more depleted

[Hoheisel and Schmidt] We changed it in the revised manuscript.

[Referee#2] Line 294: remove the space between the first parenthesis and “see”

[Hoheisel and Schmidt] We corrected it in the revised manuscript.

[Referee#2] Line 331: go one step further → extend the effort?

[Hoheisel and Schmidt] We changed it in the revised manuscript.

[Referee#2] Line 378: This is supported by the fact that the amount of emissions from sectors, such as livestock farming, with well studied emission factors and accurate statistical data are comparable for both inventories → This is supported by the fact that the amount of emissions from sectors with well studied emission factors and accurate statistical data are comparable for both inventories, such as livestock farming, are comparable for both inventories.

[Hoheisel and Schmidt] We corrected this in the revised manuscript.