Author's Response to Referee#1 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#1 for the detailed and constructive comments and their useful suggestions. We have revised the manuscript accordingly.

General Comments:

[Referee#1] The paper "Six years of continuous carbon isotope composition measurements of methane in Heidelberg (Germany) – a study of source contributions and comparison to emission inventories " is a detailed analysis of observed methane mole fraction and carbon isotope signature in Heidelberg, supported by elaborated discussion of possible origin of observed methane elevation and comparison with existing inventories. The paper focus on observed trend in methane mole fraction and carbon isotopic signature over 6 years and the title clearly reflect the contents of the paper. Also, an abstract provides a concise and complete summary. Overall presentation is well organised and deliberated, and the used language is fluent and precise, making the paper easy to follow and understand. The paper can be treated as case study of methane long-term observation in the urban area. Overall, the paper address relevant scientific questions within the scope of ACP and presents novel data with its interpretation, which are useful to the atmospheric community. The substantial conclusions are reached, showing the long-term trend and similarities and discrepancies with other atmospheric studies and inventories. The scientific method and assumptions are clearly outlined. The specification of measurement site and used instrument (Allan deviation, long-term reproducibility, accuracy based on comparison with MPI-BGC measurements) is well described.

However, there is not too much explanation of used Miller-Tans method, especially there is no information about extracted background and its potential impact for determined δ13C signature of methane source. More elaborated description of comparison between Keeling and Miller-Tans would be also useful. Also, giving more details about implementation of Miller-Tans method will make results more traceable and reproductive.

Overall, the paper is well balanced, clear and, containing appropriate references and gives important contribution to atmospheric studies of methane. Some questions and comments should be taken into consideration before publishing.

Specific comments:

[Referee#1] The more detailed explication of used Miller-Tans method in this study is missing. What was background used in Miller-Tans method? How the background was chosen and how the choice of background could affect obtained values using Miller-Tans method?

Line 182: What tests was made to compare Keeling and Miller-Tans methods? Also, could you elaborate more about the fact you did not observe differences between Keeling and Miller-Tans method? There are studies showing that the differences are observed using these two different methods.

[Hoheisel and Schmidt] Thank you for your detailed comments and questions regarding the Miller-Tans and Keeling plot methods. Your comments have shown us that we were not clear in the manuscript and that the term "Miller-Tans method" can lead to confusion.

In our study, we used equation 5 derived from Miller and Tans (2003):

$$\delta_{obs} \, C_{obs} = \delta_s \, C_{obs} + C_{bg} \, (\delta_{bg} - \delta_s)$$

In this form of the 'Miller-Tans method', the background values can remain unknown and must not be specified. This is different in equation 6 from Miller and Tans (2003), which we did not used.

In addition to the 'Miller-Tans method (equation 5)', we also used the Keeling plot method to determine the mean isotope source signatures. A comparison between the mean isotope source signatures calculated with the 'Miller-Tans method (equation 5)' and the Keeling plot method using the York fit (York et al., 2004) showed no significant difference. All our results are identical in more decimal places than the significant digits.

Since we tested both the 'Miller-Tans method (equation 5)' and the Keeling plot method in our study, and all results are identical regardless of which of the two methods was used, we have decided to explain our results using the Keeling plot method rather than the 'Miller-Tans method'. We have made the necessary changes in the revised manuscript and hope that the used methods are now clearer and the results of our study more traceable.

[Referee#1]	Why KuMF results were included in section 3.6 but not in section 3.5? How monthly δ^{13}C-CH$_4$ signatures from inventories were calculated?
[Hoheisel and Schmidt]	Emissions from KuMF are always included in the LUBW inventory. Emissions from the same sources have different sector names in the EDGAR and the LUBW inventories. The 'small and medium-sized combustion plants (KuMF)' sector reported by LUBW and the 'energy for buildings' sector from EDGAR describe the same emission category. Therefore, in accordance with the EDGAR inventory, the KuMF sector was referred to as 'energy for buildings' when comparing both inventories. When describing the preparation of the artificial monthly LUBW data, we have used the term KuMF to make it clearer which LUBW sector we have used. We understand, that this can lead to confusion. Therefore, we have changed the paragraph in the revised manuscript. To determine the monthly mean δ^{13}C-CH$_4$ isotopic source signatures, we assign a source-specific isotopic signature to the monthly emissions from each sector. EDGAR already reports monthly CH$_4$ emissions. Since LUBW only reports annual emissions, we determined monthly values by dividing the annual values for each sector by 12. We then included an annual cycle in the emissions of the energy for buildings (KuMF) sector, analogous to the annual cycle reported by EDGAR.

"EDGARv6.0 reports monthly CH$_4$ emissions, which were used to calculate the monthly mean isotopic carbon source signatures. The most prominent annual cycle in the CH$_4$ emissions estimated by EDGARv6.0 occurs in the energy for buildings sector. The LUBW only reports annual emissions. Therefore, we included a modelled annual cycle for the energy for buildings sector (the LUBW sector small and medium-sized combustion plants - KuMF). This modelled annual cycle is based on the annual cycle noticeable in the monthly EDGARv6.0 emissions for the energy for buildings sector."

[Referee#1]	Discussion about discrepancies between measurements and inventories in other cities, including comparison with Heidelberg is worth to add.
[Hoheisel and Schmidt]	Thank you for the comment. We agree that it is a valuable contribution to our analysis, to include results of other studies in cities, which also analyse the discrepancies between measurements and inventories. We have included this in the revised manuscript.

[Referee#1]	Line 30-35 Given range of microbial and thermogenic is narrower than in the literature (e.g. Menoud et al, 2022) and not overlapping as it is observed during source signature studies. Please clarify.
[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 $\delta^{13}C$-CH_4 values of the different source categories are not always as distinct as indicated above. They give much larger ranges of $\delta^{13}C$-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#1]	Line 42- 45: It would be also worthy to include and cite paper of Rennick et al 21 (https://doi.org/10.1021/acs.analchem.1c01103) as it is another laser spectrometry method for methane isotopes measurements.
[Hoheisel and Schmidt]	We have included the study in the revised manuscript.

[Referee#1]	Line 121 Could you add short description (e.g., one sentence) to explain principal of CCGCRV?
[Hoheisel and Schmidt]	Thank you for pointing this out. We have added a short description of CCGCRV in the revised manuscript:

"*CCGCRV can be used to decompose a time series into a trend and a detrended seasonal cycle by fitting a polynomial equation combined with a harmonic function to the data and applying a filter to the residuals. In this study, we used 3 polynomial terms and 4 annual harmonic terms. The short- and long-term cutoff values for the low-pass filter are 80 and 667, respectively.*"

[Referee#1]	Line 146: What is frequency of used Mace Head data? What is the height of the inlet in Mace Head? Why Mace Head was used?
[Hoheisel and Schmidt]	We used monthly mean Mace Head data and included more information 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 the Mace Head Observatory is not optimal as a background station for Heidelberg. However, since this is the only background station west of Heidelberg with a long published $\delta^{13}C$-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#1]	Line 177: Why Allan standard deviation was used as uncertainty instead of standard deviation?
[Hoheisel and Schmidt]	In the Miller-Tans/Keeling plot approach, we perform a York fit that includes the uncertainty in x and y. To determine these uncertainties, we used the Allan standard deviation instead of the standard deviation to account for instrumental uncertainty rather than atmospheric variability included in the averaged value.

[Referee#1]	Line 209: Why the method to extend for another hour, up to 12 hours was chosen? Why 12 hours was chosen as criteria to exclude data?
[Hoheisel and Schmidt]	For the moving Miller-Tans/Keeling plot approach, we tested two scenarios: We started with 1 hour and increased the interval by hourly steps if our criteria were not met, and additionally, we started with a 12-hour time window and decreased it by hourly steps if our criteria were not fulfilled. We noticed no significant difference between the monthly averaged mean isotopic source signatures calculated from the two scenarios. Since we are interested in short-term events, we presented the scenario where we extended the time window.

[Referee#1]	Line 205-214: The one minute step seems quite small, especially that some pollution peaks can last longer. You mentioned you averaged all values directly adjacent in time. Was it done manually? Is it enough valid method to separate individual pollution event? Would wider step (e.g., few minutes) be more adequate?
[Hoheisel and Schmidt]	We automatically applied the moving Miller-Tans/Keeling plot approach to the complete time series of six years. For each time, we chose the smallest time interval for the moving Miller-Tans/Keeling plot, which fulfilled our criteria. Therefore, we achieve results for 18% of the one-minute averaged data. Based on your comments and the ones from Referee#2, 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 examine the hourly and daily averages of the results of the moving Keeling plot. We changed this in the revised manuscript accordingly.

[Referee#1]	Line 235-245: First you say there is no significant trend in the monthly mean $\delta^{13}C$ isotopic signatures, while later you describe visible differences between signatures for individual months. Please clarify.
[Hoheisel and Schmidt]	As mentioned in the manuscript, for each approach individually, there is no significant trend detectable in the monthly mean isotopic carbon source signatures between 2014 and 2020. However, when comparing the monthly mean isotopic carbon source signatures determined from different approaches, we can notice differences in individual month and in the annual cycle.

[Referee#1]	Line 262-267: Could choosing the wider step than 1 minute could remove possible artefact of averaging and give more reliable values to determine diurnal cycle?
[Hoheisel and Schmidt]	For each time x, the mean isotopic source signature is determined by applying the Miller-Tans/Keeling plot approach to the minutely-values in a 1 to 12 hours interval around the time x. Choosing a wider step of several minutes instead of one minute would only decrease the number of resulting mean isotopic source signature values, but should not change the monthly averages significantly. Furthermore, we also tested to average the measured atmospheric CH_4 and $\delta^{13}CH_4$ values to 5 or 10 minutes instead of 1min and found no decrease in the error of the determined mean isotopic source signatures.

[Referee#1]	Line 271: First you said it is not possible to get reliable results on diurnal cycle then in line 271 you say, "This indicates that the composition of CH_4 sources in Heidelberg is the same during day and night". It seems to be contradictory. Please clarify, also regarding impact of the instrument precision for diurnal measurements.
[Hoheisel and Schmidt]	The mean isotopic source signature determined with the moving Miller-Tans/Keeling plot approach does not provide us with results to reliably resolve diurnal cycles. A higher precision of the instrument would make it possible to obtain mean isotopic signatures even for small CH_4 ranges with small fitting errors. Thus, more mean isotopic source signatures will match the chosen selection criteria for an interval of a few hours, and thus a higher temporal resolution is possible.
	Later in the manuscript, we compared the monthly mean isotopic source signatures obtained with the night-time and the moving Miller-Tans/Keeling plot approach. The first approach uses only the nighttime measurements, while the second approach uses daytime and nighttime data. As we could not find a significant difference between the two methods, we concluded that this could be caused by two possibilities: First, there is no difference in the composition of emissions between day and night, and second, the moving Miller-Tans/Keeling plot approach is influenced mostly by the nighttime increase.

[Referee#1]	Line 288: Do the monthly approach and moving Miller-Tans approach represent the same catchment area (both bigger than night-time approach? If yes, this hypothesis does not explain differences in results from monthly and moving Miller Tans approaches. Please comment.
[Hoheisel and Schmidt]	It is likely that the monthly approach and the moving Miller-Tans/Keeling plot approach do not represent the same catchment area, which may explain the differences observed in the two approaches.

[Referee#1]	In table 1., $\delta^{13}C$-CH_4 for road transport comes from Levin et al. 1993. Is it possible this value changed over last 30 years as different cars are used now and then (e.g. diesel versus petrol, better technology etc)? Is it possible the inventories results are biased comparing to atmospheric results due to unaware shift between used δ13C-CH4 from previous studies and real values?
[Hoheisel and Schmidt]	Yes, it is true that the composition of diesel compared to gasoline and the technology in cars has changed over the last 30 years. Therefore, the $\delta^{13}C$-CH_4 value for road transportation may also have changed since then. Unfortunately, there are only a few new studies on $\delta^{13}C$-CH_4 measurements on car exhaust gases in Europe. The few values range between -20‰ (Menoud et al., 2022 measured in Hamburg in 2022) and -28‰ (Levin et al., determined in Heidelberg in 1999). We assume that the 13CH4 values of car exhaust gases are in this range. And thus, we chose the value of -22.8‰, which was reported by Levin et al. (1993). Chanton et al. (2000) describe $\delta^{13}C$-CH_4 values between -22‰ and -9‰ for 16 vehicles sampled in the United State. The value of -22.8‰ chosen by us is in the lower range.
	If we assume that the $\delta^{13}C$-CH_4 value for road transportation is -9‰ or -28‰ instead of -22.8‰, the annual mean isotopic carbon signatures, determined from LUBW/EDGAR data, change by 0.38‰/0.08‰ or 0.04‰/0.03‰. This is due to the fact that CH_4 emissions from road traffic are only a small part of the total CH_4 emissions of 2.1% and 0.6% in the LUBW and EDGAR inventory. Although the actual $\delta^{13}C$-CH_4 value for traffic today may differ from the value used in this study, this has no essential impact on our results.

[Referee#1]	Line 295-297: "the nearby CH_4 sources are more often natural gas leaks, wastewater, traffic, or emissions from energy for buildings. These CH_4 emissions are on average less depleted." – it sounds like wastewater is also less depleted, in the same category as other mentioned sources. Based on Tab 1, it is clear they are more depleted, as other microbial sources.
[Hoheisel and Schmidt]	Yes, this sentence was misleading. We changed it in the revised manuscript.

[Referee#1]	Line 390: What is the difference between value from Widory et al. (2006) and "publications describing ^{13}C for CH_4 emitted by waste incineration in the way we needed them to calculate the mean $\delta^{13}C$-CH_4 isotopic source signature" What is the "needed way" and how it is different from method presented in Widory et al. (2006)?
[Hoheisel and Schmidt]	During the development process of the paper, the paragraph in line 390 changed several times, so that in the end it unfortunately became misleading and imprecise. We just wanted to express that despite extensive literature research we have not found a study that has determined and reported the $\delta^{13}C$-CH_4 isotope signature of waste incineration. Thus, we adopted the ^{13}C composition of waste incineration reported by Widory et al. (2006) for CO_2. We have changed the sentence in the revised manuscript.

[Referee#1]	Line 415-420: Repeating annual mean results here brings some confusion. I suggest removing it and focus only on annual cycle in this paragraph.
[Hoheisel and Schmidt]	Thank you for your suggestions. We have slightly changed the structure of the subchapter in the revised manuscript to make it easier to follow.

Technical corrections:

[Referee#1]	Line 30 and further: δ13C-CH4 should be given in order from smaller to bigger, e.g., (-70 ‰ to -55 ‰) instead of (-55 ‰ to -70 ‰).
[Hoheisel and Schmidt]	Thanks, we changed it in the revised manuscript.

[Referee#1]	Figure 9: Remove too at the end of last sentence
[Hoheisel and Schmidt]	Yes, we removed it in the revised manuscript.

[Referee#1]	The link to access used data does not work.
[Hoheisel and Schmidt]	We are still working on the public permanent DOI to the measured Heidelberg data. So far, we have provided a preliminary DOI for the editor and the reviewers to the editor.