

Author's responses to reviewer's comments follow. A copy of the reviewer comment is given (with comment 'number') followed by a response (blue font).

Response to referee 1

1. General comment

These revisions made have improved this paper. I suggest however that there is a careful grammar check before publication, in particular in the recently revised sections.

Thank you for your comments. We finalized the grammar checks and tried to improve manuscript as following specific comment.

2. The Miller Tans analysis is an improvement. The source signatures are compared with the global averages from the Sherwood et al. database, but it would be better to compare with signatures for the regions, as isotopic signatures for the sources can vary regionally (e.g. Ganesan et al., Spatially Resolved Isotopic Source Signatures of Wetland Methane Emissions - Ganesan - 2018 - Geophysical Research Letters - Wiley Online Library).

Thank you for the suggestion. We added the sentence below.

P22 L6: Regionally CH₄ emissions from wetlands in Siberia are at $-69.9 \pm 5.5\%$ while Hong Kong was more enriched at $-56.9 \pm 3.8\%$ (Ganesan et al., 2018). In northern China, a high coal emission area, heavy CH₄ signal appears from -35% to -50% (Feinberg et al., 2018).

Feinberg et al.(2018): Isotopic source signatures: Impact of regional variability on the $\delta^{13}\text{C}_{\text{CH}_4}$ trend and spatial distribution, Atmos. Environ. <https://doi.org/10.1016/j.atmosenv.2017.11.037>

3. Uncertainties in the Miller-Tans signatures were not given for the KL site (page 22, line 12).

Corrected.

P22 L14: . KL showed the quite constant values from -55 ± 1.6 to $-54 \pm 3.1\%$

4. Some of the graph axis labels do not have subscript 4 in CH₄ (figures 6 and 7).

Corrected.

5. Missing superscript 13 in δC (page 3, line 6)

Corrected.

Author's responses to reviewer's comments follow. A copy of the reviewer comment is given (with comment 'number') followed by a response (blue font).

Response to referee 2

1. General comment

I have gone through the response to my comments and the revised manuscript and found the manuscript has been improved to some extent. However, I think that there remain some problems which should be resolved before acceptance. The authors should respond the following comments before publication.

Thank you for your comments. We tried to resolve the pointed problem here.

2. I'm not sure what the sentence, "However, isotopic signature using $\delta^{13}\text{CH}_4$ explained that CH_4 sources are becoming mixture of not only biogenic but also fossil fuel sources in East Asia from 2006 to 2020", means. I believe that the CH_4 sources in East Asia included fossil fuel-related source also before 2006.

Agree. We revised the sentence below:

Abstract P1 L23-24: "However, $\delta^{13}\text{CH}_4$ indicate that the CH_4 trend in East Asia is derived from biogenic and fossil fuel sources from 2006 to 2020.."

3. The added sentence in the revised manuscript, "... since generic water correction cannot be applied to each instrument in different environments" (page 4, line 21) is a little bit misleading. The previous studies including Rella et al. (2013) and Hazan et al. (2016) indicated that the generic manufacturer's water correction function does not necessarily provides appropriate values for wet air samples. However, as Rella et al. (2013) indicated, the preliminary reduction of water vapor of sample air less than 1% allow us to measure the CH_4

mole fraction within the level of GAW's compatibility goal (± 2 ppb). So, I think it would be better for the authors to simply mention that the sample air is dried to reduce the humidity effect less than the detection limit instead of correcting the humidity effect based on the generic manufacturer's water correction function or independently determined water correction function.

Thank you for your comment. We should make clear that we don't correct our values from the humidity effects because we are using a drying system. We just consider these values as one of our uncertainty factors to show our data are not affected by humidity. And as reviewer mentioned this value is negligible. Therefore, we revised the sentence like below and hope this is acceptable.

P4 L20: This system dried the sampled air enough so that the bias from the humidity is negligible. This is described in section 2.3 and 3.1.

4. In the revised manuscript, the authors mentioned "AMY started flask sampling for CH₄ and $\delta^{13}\text{C}(\text{CH}_4)$ in December 2013 with same method like TAP and these data were used only for characterization of CH₄ at AMY in section 3.5" (page 8, line 22-23). But there is no discussion based on the $\delta^{13}\text{C}(\text{CH}_4)$ data for AMY in this paper.

There is a typo section 3.4.3 and added the data are used in Fig. S6. We revised the sentence.

P8 L23: .. and these data were used only for characterization of CH₄ at AMY in section 3.4.3.

5. The authors should explain how to prepare the Miller-Tans plots shown in Fig. 9b, Fig. 6S, and Fig. 7s because most readers are not necessarily familiar with the plot. In particular, the basic equation for the Miller-Tans plot should be described in the manuscript. And then, the authors

should clarify how to determine the background values of the CH₄ concentration and isotope ratio. Additionally, a proper reference should be cited in the manuscript for the Miller-Tans plot.

We added explanation and reference as well.

P9 L1: To understand the regional source signature of excess CH₄ and to consider background atmospheric variations, Miller-Tans plot are used with flask sample data (Miller & Tans, 2003).

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

Here, C and δ refer to CH₄ and $\delta^{13}\text{C}_{(\text{CH}_4)}$, and the subscript bg, obs and s refer to background, observed and source values. Therefore, by plotting $\delta_{\text{obs}}C_{\text{obs}} - \delta_{\text{bg}}C_{\text{bg}}$ (y) against $C_{\text{obs}} - C_{\text{bg}}$ (x), δ_s indicates the slope of the linear regression represents the source $\delta^{13}\text{C}_{(\text{CH}_4)}$ signature. For background data, we downloaded data of CH₄ and $\delta^{13}\text{C}_{(\text{CH}_4)}$, observed at Mauna Loa (<https://gml.noaa.gov/dv/data>, last access March 2022)

6. I'm not sure the discussion based on the regional isotopic signatures from the Miller-Tans plots in page 22 line 12-20. The isotopic values can give us the information about the mix of the isotopically different CH₄ sources of the regional emissions causing the excess CH₄ at TAP. Therefore, the temporal and spatial changes in the isotopic ratio probably reflect the changes in the mix of the sources. But there is no information about emission strength in the isotopic ratio for the regional emissions. Therefore, I think it is difficult to discuss the variation in the CH₄ growth rate from the result based on the isotopic analysis in this study. For example, I cannot understand why the authors conclude "This suggested that CH₄ growth rate in East Asia was affected not only biogenic but also pyrogenic sources, unlike global." (page 22, line

12-13). If the authors want to discuss the cause of the trend variation in East Asia, the isotopic ratios for the baseline should be discussed. But the authors also mentioned “The long-term trend at AMY was very similar to the global trend” (page 21, line 21-22). So, I think the trend of isotopic ratio at AYM is also similar to the global trend. The similar discussion about the trend in East Asia based on the isotopic analysis is also described in Section 4 (page 24, line14-15)

We understand what you mean but when air is collected by flasks, we consider it is well-mixed air. This means flask air samples reflects baseline air mass rather than the polluted local air. And the baseline also reflects the air not only in northern hemisphere but also in the region. Therefore, the levels can be different from global values, but growth rate can be similar to those of global (For example, -0.026% /year for Mauna Loa and -0.027% /year at AMY from 2006 to 2020). With this reason, we applied the Miller-Tans plots to figure out only regional changes as reviewer suggested previously and applied the cluster analysis. Through the Miller-Tans plot, we remove the global (or northern hemisphere) trend and variation of CH_4 and its isotope. This means our Δ values are regional values after removing background baseline of northern hemisphere (Mauna Loa). Also, through the cluster analysis, we can assess which regions are enhanced or depleted with isotope signature from 2006 to 2020.

We assure this approach is reasonable to explain of CH_4 regional growth rate base on measurement data.

7. I'm curious about whether there is seasonality in the source regions (CN, CS, and KL) affecting the observation at TAP. If there is seasonality, does it explain to some extent the differences in the isotopic ratios for the source regions shown in this study? For example, if the air masses are transported from CN to TAP during winter, it is expected that the isotopic signature would be relatively higher because the biogenic CH_4 emissions are reduced during winter.

That is true. As reviewer mentioned, CN includes summer data with only 1.6% of total data while 95% for CS. On the other hand, CN does not always include winter data. 41% of total CN data are observed in winter while 57.4% for spring and autumn. Therefore, it is difficult to explain CN is representative of winter. In the section 3.4.3, we already described the AMY's Miller-Tans plot result in winter and summer. Regardless of season, the slope of Miller-Tans plot at AMY is $-52.3 \pm 2.2\text{‰}$ in winter and $-53.7 \pm 0.7\text{‰}$ in summer as indicating depleted δC values from 2016 to 2020 (P21 L7). This result might be different from our assumption that isotopic signature in winter should be higher than summer. When we implement cluster analysis (as described in section 2.6), we can confirm the data derived from KL or stagnated condition showed the depleted δC values (closed to biogenic source signature, from -50 to -61‰) even in winter. Therefore, we can understand that CH_4 signature slope represents the source region even though we can consider the seasonal characteristics when we applied the cluster analysis. Additionally in section 3.5 we tried to explain CH_4 signature slope changes in the same cluster sector during the long-term period. Therefore, it can be less important how much winter and summer affected on this analysis.

8. I found several mistakes in English in the manuscript as some examples are shown in the followings: Page 1, line 20-21: "... growth rate increased 3.3 ppb yr-1 ..." → "... growth rate increased by 3.3 ppb yr-1 ..." Page 1, line 30: "...compared with that of other long-lived greenhouse gases..." → "...compared with those of other long-lived greenhouse gases..." Page 7, line 18: "... days moving median of of HA..." Page 10, line 2: "The BLH can was obtained ..." Page 22, line 13: "... was affected not only biogenic but also pyrogenic..." → "...was affected by not only biogenic but also pyrogenic ..."

Therefore, I think that it should be better to check the language in general.

Corrected and whole manuscript was screened by grammar checks.

9. Added sentences for Eq. 1 (page 6, line 7-9) are rather confusing. The Eq. (1) simply expresses the dilution effect caused by the water vapor (H_{act}). But I cannot understand what the sentences, "Here H_{act} is the H₂O difference between laboratory and working standards. C_{dry} is the CH₄ mole fraction of laboratory standard while $C_{dilution}$ is the expressed CH₄ mole fraction when H_{act} existed.", mean. Do the authors consider the water mole fraction in the laboratory standard is zero? If not, the exact relationship among the H₂O differences between laboratory and working standards ($H_W - H_L$), the CH₄ mole fraction of standard with H_L ($C_{dilutionL}$) and H_W ($C_{dilutionW}$) is expressed by the following equations: $C_{dilutionW} = C_{dilutionL} - 0.01(H_W - H_L) \cdot C_{dry}$ Or $C_{dilutionW} / C_{dilutionL} = (1 - 0.01 \cdot H_W) / (1 - 0.01 \cdot H_L)$, where C_{dry} represents the dry CH₄ mole fraction of the standard. However, I think above discussion is too detailed. In the manuscript, it would be better to simply examine the absolute H₂O mole fraction of the standard gases and the dried air samples and discuss the dilution effects according to Eq. (1). I believe that the resultant changes in the CH₄ mole fractions caused by the H₂O dilution effect are negligible.

Once again, we don't apply drying correction to our data because the air is dried enough with our drying system. Therefore any result will not be changed in the manuscript.

We were keen to follow the reviewer's comment as long as we can and finally revised the sentences like below. Hope this is well reflected as following reviewer's comment.

P6 L1: where C is the CH₄ mole fraction and H_{act} is the water mole fraction difference between laboratory and standard gases (in %). For example, 0.00054% H₂O difference between two cylinders causes 0.01 ppb bias at 1800 ppb.

10. Page 5, line 28: The URL <https://gml.noaa.gov/ccl/service.html> should be <https://gml.noaa.gov/ccl/services.html>.

Corrected

11. Page 23, Fig. 9(a): It would be better to clarify the boundaries of the northern China (CN), southern China and Korea local (KL) in the map.

Corrected