

Final response by Taku Umezawa on 18 July 2012

We are grateful to both referees for their effort and comments which will significantly improve this paper. We therefore present our reply in the following (*referee's comments are in bold and italics*).

## **1. Response to Referee #1**

*This paper by Umezawa et al. presents and analyses an original dataset of methane and its stable isotopes ( $^{13}\text{C}$  and  $\text{D}$ ) acquired through commercial aircraft flights over the Western Pacific between 2005 and 2010. Such data are rather rare and can be useful to distinguish the different source types of atmospheric methane, the second anthropogenic greenhouse gas and a precursor of Ozone. In this sense the existence and the reporting of these data is highly valuable for the reduction of the uncertainties on the regional methane emissions and sinks, especially downwind of East Asia where very few long-term surface measurements are available. An extra step, if the paper gets accepted in ACP, would be to make these data available for the research community as many experimental groups do now worldwide.*

The UT data will be provided after the publication of this paper. The  $\text{CH}_4$  mixing ratio data can be provided by the CONTRAIL PIs (T. Machida, H. Matsueda and Y. Sawa) according to the CONTRAIL data protocol (<http://www.cger.nies.go.jp/contrail/protocol.html>). For the  $\text{CH}_4$  isotopic ratio data, please send your requests to T. Umezawa and S. Aoki (Tohoku University) as well as to the CONTRAIL PIs. For the  $\text{CH}_4$  mixing ratio and isotopic ratio data obtained by using ships in the LT, you could contact to T. Umezawa and S. Aoki.

### ***General comments***

*-At many places I find that the text lacks precisions and quantitative statements (see also specific comments). The introduction should be fed with more quantitative information (mean atmospheric  $\text{CH}_4$  concentration, global mean source, . . .). The authors compare different time series of concentrations ( $\text{CH}_4$ ,  $^{13}\text{C}$  and  $\text{D}$ ) but hardly*

*give any precise correlation coefficients except at the end of the paper for Keeling plots. I strongly suggest to go a bit further than XX shows weak/tight negative/positive correlation with YY and calculate correlation coefficients. The isotopic signatures also require more attention and details. Ranges of methane emissions from the different regions quoted should also appear somewhere.*

We will give correlation coefficients in the text. Also the introduction will be fed with ranges of isotopic signatures and of CH<sub>4</sub> emissions in Asia.

*-The CH<sub>4</sub>+Cl reaction in the marine boundary layer is still a matter of debate. The fact that this reaction has little impact on D and CH<sub>4</sub> but stronger impact on <sup>13</sup>C is very interesting. I suggest the authors push more the analyses on this topic. Can you give an order of magnitude of the global sink from Allen 2007 ? For the Pacific ? Do the authors see time periods or latitudinal zones where this reaction is detected in the reported data ? It is not clear why the lack of tropical intercept is an element consistent with the CH<sub>4</sub>+Cl reaction, please clarify. More (and more clear) explanations on this topic would be an improvement for the paper*

According to this suggestion, we will enrich our discussion on the CH<sub>4</sub>+Cl reaction. Also we will correct the sentences stating the importance of the reaction.

Analyzing the LT data in the SH, we found a large apparent KIE, as observed at Baring Head, New Zealand and Scott Base, Antarctica by applying the “phase ellipse” analysis (Allan et al., 2001, 2005). However, we need a longer data record to characterize the phase ellipses and quantify the contribution of the CH<sub>4</sub>+Cl reaction. We will report complete descriptions of the ship observations in our future publication.

For the implication from the latitudinal distributions, we would mention that pushing the  $\delta^{13}\text{C}$  in the LT down by 0.05‰ for the whole observation latitudes could have resulted in the profile with intersection. Only 2 ppb contribution by the Cl reaction could explain this value, taking account for the large KIE of the reaction. We do not upscale this value (2 ppb) globally, since it requires uncertain assumptions.

*Specific comments*

***P9036-123-26 : please give mean concentration and ranges of global emissions.***

We will add the global average CH<sub>4</sub> mixing ratio (1794 ppb) in 2009 (Dlugokencky et al., 2011) and net emissions during 2000s (514±14) Tg CH<sub>4</sub> yr<sup>-1</sup> (Patra et al., 2011).

***P9037-119 : “wide area” I suggest to add : . . . at the cost of less precise individual measurements in regards to the high precision of surface observations”***

This will be added.

***P9038-121 : “substantial amount. . .” : please be more precise here and give ranges of emissions from the different Asian regions from the literature.***

Since quantifying each emission value for the individual Asian regions is still an active research topic, we will give ranges of CH<sub>4</sub> emissions in Asia in total. Namely, literatures give rice paddy emission of ~20–50 Tg CH<sub>4</sub> yr<sup>-1</sup>, livestock of ~26–36 Tg CH<sub>4</sub> yr<sup>-1</sup>, fossil fuel consumption of ~10–20 Tg yr<sup>-1</sup>, and natural wetlands of ~40 Tg CH<sub>4</sub> yr<sup>-1</sup> (see references in the revised text).

***P9039-13 : “characteristic signature”: please use isotopic signatures instead.***

This will be corrected.

***P9039-13-5 : There are ranges for isotopic signatures. Please give ranges and not only one value per type of source.***

We will give ranges of isotopic signatures reported by literatures.

***P9039-120 “almost” : Well looking at figure 1 almost is not always that close. What is the range of horizontally projected distance between UT and LT observations? It maybe more precise to quote this range instead of only almost. . .***

The horizontal distance between the UT and LT observations are less than 20° in longitude. This will be given in the text.

***P9040 : “about 1.7l” : what is the pressure of the filled flasks ? It may worth writing it in the text.***

The pressure of the filled flask is ~0.15 MPa above the surface atmospheric pressure. This will be added in the text.

***P9041-I2-5 : Why the authors did not use the international NOAA04 scale ? It would make comparison much easier. The authors should explain why there are still on their own scales.***

The TU and NIES have maintained individual scales for long years and have joined the WMO RoundRobin intercomparison program. The scale differences between NIES and NOAA are described in the WMO report (Zhou et al., 2009). The TU scale has also been cited in the paper presenting the NOAA scale (Dlugokencky et al., 2005). We believe that it is reasonable to use the TU and NIES scales in this study, since both are traceable and stable. In addition, both scales are well known to scientific community, since they have been used in many scientific papers (some of them are referred in this paper).

***P9041-I12-17 : It seems to me there is a contradiction here. NIES and TU agree with each other but round robin found different differences between TU & WMO and between NIES and WMO. Please clarify this confusing paragraph.***

We have made comparison of the TU and NIES scales several times. The latest comparison shows that the scale difference is less than 1 ppb at baseline atmospheric CH<sub>4</sub> level. This result differs very slightly from the WMO report (Zhou et al., 2009), in which both scales differ by 2.0 ppb at most. We also note, in the WMO report, that comparison between the TU and NOAA scale was made based on measurements at a different institute (AIST) following the TU scale. Direct measurements using the TU measurement system are needed and will be reported in the next WMO report in coming years. Because of this, we will take out citing Zhou et al. (2009) and describe the comparison between the TU and NIES scales.

***P9042-I15-18 : The reported drift is confusing to me. Is it a slow drift? Did it happen between two measurement periods? Please clarify this part.***

It was a sudden change happened between two measurement periods. This will be clarified.

***P9043-118 : “observed seasonal cycles. . .” how did you do that ? What stations/dataset did you use to make the choice of latitudinal bands for grouping your data ? Please be more precise here.***

The original air samplings were made at 5° latitude intervals and every sample was analyzed for CH<sub>4</sub> mixing ratio. Therefore, we inspected the CH<sub>4</sub> mixing ratio data available at 5° latitude intervals from 35° N to 40° S. The latitude bands were then determined so that the average seasonal cycles of the CH<sub>4</sub> mixing ratio at the respective observation latitudes, derived by the curve fitting technique, are similar within each band. This explanation will be added.

***P9044-14: suggested : original GLOBAL flux field***

This will be corrected.

***P9044-19 : EDGAR P9044-19: Which version of EDGAR has been used? Is it EDGAR3.2?***

This will be added.

***P9044-111 : I would use “prescribed” instead of “adopted”.***

This will be corrected.

***P9044-118 How the interpolating/extrapolating has been done for the years 2005-2010? The text is not precise enough on this.***

We extrapolate the EDGAR inventory for these years. The text will be corrected.

***P9044-125 : at “32-15” : this phrasing is not clear. Maybe write For time series between 15 and 32 N, ...***

This will be corrected.

***P9045-17 : weak negative correlation : please give a correlation coefficient***

This will be added.

***P9045-17-9 : Which latitudes are you talking about ? Please clarify.***

This part mentions latitudes between 32° and 15° N. This will be added.

***P9046-121 : “opposite phase” : what is the correlation coefficient ? There are not always in phase opposition (e.g. second half 2006, early 2008, ..). Please be more precise.***

We will add the correlation coefficient in the text. The text will be also corrected.

***P9047-18-9 : UT and LT phase opposition : it is not clear from the figure, please give a correlation coefficient and modify the text according to the computed value.***

As the referee points out, phase opposition between the UT and LT CH<sub>4</sub> mixing ratios is not always the case (they look opposite in most periods, but do not in some places). As a result, the UT and LT CH<sub>4</sub> mixing ratios were found not to significantly correlate with each other. In this sentence, we will focus on the observed high UT mixing ratios in boreal summer when the LT CH<sub>4</sub> mixing ratio shows low value.

***P9047-116 : almost in phase : please give a correlation coefficient***

This will be added in the text.

***P9048-123 : negative correlation : please give a correlation coefficient***

This will be added in the text.

***P9049-11 : see general comment on CH<sub>4</sub>+Cl . Can you see the impact of this reaction in your data ?***

We will enrich our discussion (see also our response to the referee’s general comment).

***P9049-116-18 : see general comment on CH<sub>4</sub>+Cl. Please clarify why CH<sub>4</sub>+Cl is consistent with a profile without intersection between LT and UT.***

We will enrich this part for better discussion (see also our response to the referee’s general comment).

***P9052-15-14: at this end of this paragraph quoting literature, please say whether your results are consistent with the reported studies.***

This will be added in the text.

***P9053-111-13 : It seems that the concentrations are underestimated after 2008. What do you mean by temporal change ? How do your global emissions change from one year to the next. I suggest that emissions may be underestimated in your emission scenario. Can you provide the global emissions used ?***

The global emission in our model was set to be almost constant ( $543.3 \pm 0.6 \text{ Tg CH}_4 \text{ yr}^{-1}$ ) for the observation period 2007–2010. This information will be given in the section describing the model settings. The text will be corrected to clarify that our CH<sub>4</sub> emission scenario might be underestimated.

***P9054-110-11 : Not only biogenic source are depleted compared to the atmosphere. I suggest : These values suggest a mix of source with substantial contributions from <sup>13</sup>C depleted sources such as biogenic emissions from rice paddies and livestock, . . .***

This will be corrected.

***P9055-17-8 : Please explain why Stratospheric CH<sub>4</sub> is isotopically depleted as compared to tropospheric one.***

The stratospheric CH<sub>4</sub> is actually “enriched” compared to the troposphere, since there are no CH<sub>4</sub> sources in the stratosphere and CH<sub>4</sub> is enriched by KIEs through reactions with OH, Cl and O(<sup>1</sup>D) during its long residence time in the stratosphere. This explanation will be added in the text.

***P9056-12 : idem as P9054-110-11***

This will be corrected.

***P9056 : Conclusion : I would mention a potential revolution in the field of methane isotope measurements which is the Quantum Cascade Laser instruments which may deliver continuous CH<sub>4</sub>, <sup>13</sup>C and D measurements in a near future. This would enhance the potential of isotopic observations to reduce the uncertainties on the present***

*methane cycle.*

This will be added.

*Figures : figure 2 is a bit small. It is sometimes hard to see variations.*

We hope and will request that the figure will be enlarged in the final revised paper.

## **2. Response to Referee#2**

### *General*

*The paper presents new methane data (mixing ratio,  $d^{13}CH_4$ ,  $dD-CH_4$ ) from the upper troposphere over the Western Pacific but also from the lower troposphere. The data are valuable and are interpreted following known concepts: transport of air masses, source attributions, Cl-sink.*

*The precision of data is sufficient to resolve the expected signal with standard deviations for  $CH_4$  mixing ratios of around 2ppb, for  $d^{13}CH_4$  of 0.08permil and  $dD-CH_4$  of 2.2permil. However, atmospheric signals that are within these errors should not be over-interpreted (see also specific remarks). Furthermore it would be beneficial for the weight of the paper to note regression coefficients when comparing the time series in chapter 3.*

We will be more careful for the treatment of the insignificant signals and texts will be modified. Regression coefficients will be given.

*With respect, one remark considering the GC-IRMS method: In the methodological paper by the lead author (DOI:10.2151/jmsj.87.365 ) it is described that the isotopic results are independent of the amount of injected air (above a certain threshold) while  $CH_4$  mixing ratio and matrix are kept constant. However, in this study the amount of sample was kept constant, but the  $CH_4$  mixing ratio changes. I am aware that it is difficult to assess this issue, however I want to point to the fact that matrix effects / mixing ratio effects could influence isotope numbers which is not ruled out*



*by the authors. I suggest to mention this issue in the paper or even better assess it experimentally.*

Description of this issue will be added. After Umezawa et al. (2009), we made additional tests to examine the linearity of our system. The results showed that measured values are invariable if peak heights of the IRMS chromatogram are more than 3 and 2.5 V for  $\delta^{13}\text{C}$  and  $\delta\text{D}$ , respectively. These threshold values correspond to about 800 and 1100 ppb in sample air of 100 mL volume. All measurements presented in this study had higher  $\text{CH}_4$  mixing ratio than these thresholds and thus higher peak heights, allowing us to make no corrections for the linearity effect.

However, as the referee mentioned, we have not made any tests with respect to change of the  $\text{CH}_4$  mixing ratio, keeping sample volume constant. For this purpose, we need a set of cylinders of different  $\text{CH}_4$  mixing ratio but the same isotopic ratios, as very recently presented by Sperlich et al. (2012, Atmos. Meas. Tech. Diss.). Unfortunately we do not have such set of gases and it is difficult to assess this issue at this moment.

Sperlich, P., Guillevic, M., Buizert, C., Jenk, T. M., Sapart, C. J., Schaefer, H. and Blunier, T.: A combustion setup to precisely reference Atmospheric Measurement Techniques Discussions, 5, 3499–3518, 2012.

*In some parts of the manuscript structure and English language could be improved to result in a more concise paper.*

We will make efforts to improve the structure and English language.

### *Specific*

***p9042: Point out that the “test gas” is basically your reference that you use to calibrate  $d^{13}\text{CH}_4$  and  $d\text{D-CH}_4$  to the international scales (VPDB and VSMOW). Give the information how the isotope values of “test gas” have been determined in the first place. This is important as the pure  $\text{CO}_2$  and  $\text{H}_2$  used as working standard gas are not suitable for referencing (“identical treatment” - principle: Werner, R. A. & Brand, W. A. Referencing strategies and techniques in stable isotope ratio analysis Rapid Communications in Mass Spectrometry, 2001, 15, 501-519)***

For  $\delta^{13}\text{C}$  measurements of sample air, we determine measured value relative to our working standard of pure  $\text{CO}_2$  stored in a high-pressure cylinder that was calibrated using a dual-inlet IRMS against the V-PDB scale. Thus, our reference is this pure  $\text{CO}_2$  cylinder, not the test gas. In this sense, our  $\delta^{13}\text{C}$  measurements do not follow the IT principle. The test gas is used for monitoring stability of our system and has showed our system has good reproducibility even in a long view.

On the other hand, our  $\delta\text{D}$  measurements were made by referencing the test gas value, as the referee pointed out. Therefore, we can call the test gas as our reference and our daily measurements of sample air follow the IT principle. However, at the first place, we determined the isotopic value of the test gas using our GC-C/P-IRMS system referencing pure  $\text{H}_2$  cylinder that was calibrated using a dual-inlet IRMS against the V-SMOW scale when our system was quite stable.

We will add the above information. As the referee assumes, experimental set up, which will enable us to follow the IT principle, as well as intercomparison with external laboratories are important future challenges.

***L22: Tell us which conclusions you drew following the Bock 2010 reference?  
Considering pyrolysis conditions you could additionally cite: Brass, M. & Röckmann, T. Continuous-flow isotope ratio mass spectrometry method for carbon and hydrogen isotope measurements on atmospheric methane Atmos. Meas. Tech., Copernicus Publications, 2010, 3, 1707-1721***

A ceramic tube used as a pyrolysis furnace “ages” with characteristic changes. Through further experiences with our measurement system after the paper Umezawa et al. (2009), we have been aware of it and introduced a check up and maintenance for the pyrolysis condition, which is very similar to those documented well in Bock et al. (2010) and Brass and Röckmann (2010). We will add this information.

***P9047 L20-p9048 L2: Maybe it would be beneficial to elaborate a bit more on the mentioned seasonally varying air transport in this section.***

We will describe more about the location of the intertropical convergence zone (ITCZ) and its possible effect on the  $\text{CH}_4$  observations in the latitude band of interest ( $5^\circ\text{N}$ – $10^\circ$

S). The ITCZ travels northward in boreal summer and vice versa in winter, which plays important role in trace gas observations in the region.

***P9051 L15-22: considering the analytical precision of 0.08permil for d13CH4 and 2.2permil for dD these numbers should be considered constant.***

This will be incorporated.

***P9053 L26 to p9054 L 5: There is no significant difference for CH4 mixing ratios (difference = 23 and 31 ppb), d13CH4 (difference 0.12 and 0.14permil) nor dD-CH4 (difference 3.0 and 3.2 permil) from both South/East Asia compared to baseline. This should be mentioned.***

We will mention to the small differences the referee pointed out.

***p9054 L6 et seqq: Consequently, the Keeling approach will give a similar result for all source areas. The end member for baseline should be given for a comparison, to make this clear to the reader.***

We will take out the Keeling plot values and add end-member values for the baseline.

***Technical***

***p9044 L9: EDGAR instead of EDGER***

This will be corrected.

***p9064 L22: Aircraft instead of Aircrat***

This will be corrected.

***p9052 L24: after UT: mention (Table 1 and Figure 1).***

This will be added.