

Interactive comment on “Carbon and hydrogen isotopic ratios of atmospheric methane in the upper troposphere over the Western Pacific” by T. Umezawa et al.

Anonymous Referee #2

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General

The paper presents new methane data (mixing ratio, $d^{13}\text{CH}_4$, $d\text{D-CH}_4$) 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 $d^{13}\text{CH}_4$ of 0.08permil and $d\text{D-CH}_4$ 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

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weight of the paper to note regression coefficients when comparing the time series in chapter 3.

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 CH₄ mixing ratio and matrix are kept constant. However, in this study the amount of sample was kept constant, but the CH₄ 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.

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

Specific

p9042: Point out that the “test gas” is basically your reference that you use to calibrate d¹³CH₄ and dD-CH₄ 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 CO₂ and H₂ 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) 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

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

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

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. 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.

Technical

p9044 L9: EDGAR instead of EDGER

p9064 L22: Aircraft instead of Aircrat

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

Interactive comment on Atmos. Chem. Phys. Discuss., 12, 9035, 2012.

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