

Interactive
Comment

***Interactive comment on* “The isotopic composition of methane in the stratosphere: high-altitude balloon sample measurements” by T. Röckmann et al.**

Anonymous Referee #1

Received and published: 22 June 2011

Review of paper by T. Roeckmann et al.

The paper presents and discusses in detail the isotopic composition of methane measured in balloon-borne air samples collected between ~ 6 and ~ 35 km, i.e. largely in the stratosphere. Indeed, the dataset originating from very different latitudes and seasons and encompassing a time period of 16 years is impressive and by far tops the few data points published so far. Moreover, the analysis goes in depth and the first author is a well-recognized expert in atmospheric isotope studies. However, I have two major concerns and many minor ones (see below) and thus cannot support publication in the present form, yet.

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

Major concerns

(1) Poor presentation and clarity

I have to admit that I never spent more time to review a manuscript than with this one. And indeed this is only partially due to the complexity of the topic! Often I could not follow how or based on what equations, resp., certain findings or numbers have been inferred. Frequently and I would even say mostly, the actual (mathematical) analysis of the data starting from the raw data to a certain result is not given. In the first sections (primarily in section 5) many equations are given and this is fine. However, later in the discussion, simply the results are shown and mostly I could not decipher what equations were used and how they were combined for the interference of the results. Almost ever, sentences such as “Based on equation X and Y and inserting the data Z shown in . . .” are missing. This makes the reading and understanding of the manuscript and most importantly the assessment extremely difficult.

This lax presentation already starts in section 5 where the theoretical basis for interpreting the data is given. Often the equations are simply given. Either the derivation of the equations or the relevant citations where the derivation is given are missing. In section 5, altogether four different epsilons are introduced, i.e. ε_{app} , ε_{mix} , ε_{eff} , and $\varepsilon_{\text{Rayleigh}}$. The definition of these epsilons is missing, and is ε_{app} not identical with ε_{mix} ? I ever understood more or less what is meant, but this “more or less” is too little for a scientific paper.

The same shortcomings apply to the table and figure captions. Often I understood what is displayed in a figure only when I have read the relevant text which ever took another 30 seconds to find it. The captions should at least be so complete that a reader can immediately understand what is plotted and what the lines and dots are. In conclusion, all this makes it very difficult and I would even say almost impossible to fully understand the paper and (important for the authors) to appreciate the work. I estimate that no more than 15-20 experts worldwide are more familiar with this iso-tope

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper



stuff than I am. If already I have so many problems what is with all the other potential readers? Please, dear authors, make the paper more digestible!

(2) Data interpretation

I strongly question the derivative of the relative sink fractions a . There are a very important point which is in my opinion not adequately considered. The major decomposition of CH₄ molecules in terms of molecules s⁻¹ cm⁻³ occurs above 30 km. That is, the CH₄ loss rate in terms of ppmv s⁻¹ cm⁻³ will peak in the upper stratosphere (>40 km) and is very small and even almost negligible below 30 km. This means in turn that the CH₄ oxidation below 30 km, although it is not negligible (i.e. $a < 30 \text{ km} \gg 0$), cannot be seen in the data collected below 30 km. As the transport (or turnover) time at 30 km is still a factor of ~ 5 shorter than the chemical lifetime of CH₄, below 30 km the CH₄ concentration and isotope composition is almost exclusively determined by transport, namely by the mixing of CH₄ imported from the troposphere and CH₄ isotopically modified above 30 km. Between the tropopause and ~ 30 km we will thus largely see a slope equilibrium between two mixing reservoirs, which explains the very uniform and compact ¹³C-D plot (Figure 3). The upper reservoir strongly changes with latitude and in case of the polar latitudes with season. This change is nicely visible e.g. in Figure 1. Dear authors, I absolutely appreciate your efforts to retrieve meaningful results (and >50% of the paper deal with this endeavor), but in my opinion a significant fraction of these efforts goes in a wrong direction. Consider that more than 90% of the data originate from below 30 km, i.e. from the two-member controlled mixing region or slope equilibrium region, respectively.

I certainly realized that you are beware of the mixing controlled layer (section 2 and 5.2.2), but in my opinion you largely did not consider it in the interpretation of the data. Indeed, many approaches for the data interpretation are fine, but the interference of the a 's is in my opinion not allowed in the present form, namely that you try to interpret a mixing line/curve as it would be due to chemistry (although I agree that the upper end member is – besides dynamics/mixing – strongly affected by chemistry).

C5267

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper



Minor concerns

p.12040, I.14 and p.12041, I.14. You should at least mention that CH₄ photolysis is a further loss channel which is in the mesosphere even very important.

Section 2. The first paragraph is not state-of-the-art. There are many newer publications e.g. by K. Rosenlof or just check the paper by H. Bönisch (Atmos. Chem. Phys., 11, 3937–3948, 2011). Distinguish between STE <380 K (with TTL) and above.

Isentropic mixing is physically impossible. Thus, write e.g. “mixing along isentropes” in the entire paper.

I.15. Define TLL

Is the entire last paragraph (I.7-I.29) necessary? In my opinion not!

p.12044, I.23. “... relative to a laboratory standard”. What is the total uncertainty of the data?

p.12046, I.13. You cannot write “STE is minimal in autumn”. First T-to-S transport is even maximal in late summer and autumn and as the PV-gradient across the tropopause is minimal in late summer and autumn, also the transport from the LMS into the tropopause is significant. Only the transport “overworld air” into the troposphere is weak in autumn.

p.12047/12048. Once you write $\delta^{13}\text{C}(c)$, in equation 1 only $\delta^{13}\text{C}$. Make it uniform!

p.12049, I.4. “Pure Rayleigh fractionation would show a slightly increasing ...”. I don't understand this. As D is associated with much stronger fractionation, continuous fractionation would lead to successively smaller changes in δD than in $\delta^{13}\text{C}$ which results in decreasing slopes, as observed.

p.12050, equation 2. As in case of almost each equation in section 5 and mentioned above, either citations or the derivative of the equation is missing.

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper



p.12052, l.9. Is “Rayleigh plot” a well-known expression? I know the Keeling plot, but you mean simply δ -value vs. concentration, right? Please clarify this that everyone can understand what is meant.

p.12052, equation 8. That’s a strange equation. What is the “i” for?

Section 5.2.1. and 5.2.2. These two sections are not felicitous. The headers say more than the text, i.e. the text and the equations do not well describe the different influences of “diffusive mixing” and “two-end-mixing” on the isotopologues. I have also general problems with these two types of mixing processes, see my comment to section 6.3. below. Also the altogether four used ε ’s (ε_{eff} , ε_{app} , ε_{mix} , $\varepsilon_{\text{Rayleigh}}$) are badly defined, i.e. what fractionation they describe and their relation gets not clear.

Fig. 4 I don’t understand, at all. Where are the end-members (p.12054, l.23)? Fig. 4 is badly explained, also the figure caption is pure.

p.12055, l.17. “.. decrease linearly” add “as observed (Figure 1)”.

p.12055, l.18. “is then mixed” exchange with “should mix”

Section 5.2.3. In this section the theoretical framework introduced before should be explained based on an example, right? . . . and indeed this is mandatory! Please also conclude that $f_{\text{diffusion,min}} = 0.5$ and that additional large-scale mixing can lead to $f < 0.5$ (which is somehow written before, but as criticized before can hardly be understood by non-experts).

Section 6.2, Fig.10. I don’t see a significant correlation for ε_D . Give the slopes and the correlation factors.

Section 6.2, Fig.11. Is it true, that you calculated the ε ’s by successively omitting data points, starting with the highest CH₄ mixing ratios? A point in Fig. 11 plotted at CH₄ = 1000 ppbv symbolize a calculation where all data points below 1000 ppbv have been considered? Please explain it more clearly. Again I don’t see a significant correlation for ε_D .

[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)[Discussion Paper](#)

Section 6.3. As mentioned before (major concern 2) the entire discussion of the observed KIE or ε , respectively, is in my opinion wrong. For instance, sentences like "...correlations result from a balance between fractionation due to chemical loss and mixing processes, primarily eddy-diffusion" (p.12061, l.20) are only half-true. Indeed the major process that causes the mixing line is "two-member-mixing". You cannot simply distinguish between this two-member-mixing and diffusive mixing. One property of two-member-mixing is that the two reservoirs mix down to very small, i.e. finally molecular scales. This final mixing step where all spatial structures disappeared, you call "diffusive mixing". I don't like this differentiation. This two-member-mixing is simply a successive mixing where the spatial scales get smaller and smaller, see e.g. Lovejoy et al. Atmos. Chem. Phys., 9, 5007–5025, 2009.

Equation 21. You mean ε , not KIE. You have at least shortly to explain why these modelled ε 's are much larger than the observed ones and have to refer to the relevant parts in chapter 5.

p.12064 and Table 7. As criticized in major concern 1 and which applies to many tables and figures, I don't see how the calculation is done for Table 7.

p.12064, l.27 ff. As written before, you cannot expect a "fairly realistic sink partitioning". The entire discussion from here on is in my opinion wrong.

In this respect, I don't understand section 7.3, at all. More than 90% of your data are from below 30km and you write "... the lower stratosphere, which is not accessible from the stratospheric measurements" (p.12065, l.24)???

Please, reassess your entire interpretation of the "global KIEs"!! You have to give really good arguments for your analysis; otherwise I get strong problems to support your paper.

Appendix A. The paper is in any case very long, complicated and hard to read. In this respect, is this appendix really necessary? I haven't learnt much and the information

[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)[Discussion Paper](#)

you can also purchase in two sentences where you explain what approach leads to a lower limit of aOH.

Interactive comment on Atmos. Chem. Phys. Discuss., 11, 12039, 2011.

ACPD

11, C5265–C5271, 2011

Interactive
Comment

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

C5271

