Answer to the referee # 3

May 4, 2018

Dear referee,

we thank you for the comments on our manuscript, which we answer point-by-point below. Page numbers relate to the discussion paper.

Major comments

> The most important thing: reading this paper might lead the reader to conclude that the assumption that dCH4/dH2O = 2 is not a good one. In fact, we have many observations (they are referenced in this paper) that show it is an excellent assumption throughout most of the stratosphere. I agree that the assumption breaks down at high altitudes.

Yes, indeed, we show that assuming a constant $\gamma_{H_2O} = \frac{\frac{d}{dt}[H_2O]}{\frac{d}{dt}[CH_4]} = 2$ is not suitable, because γ_{H_2O} changes with altitude depending on the chemical regime and OH abundance.
As explained in the introduction (page 2, lines 19–30), observations can not distinguish the H_2O produced by CH_4 oxidation from that by oxdiation of H_2, which is produced in the troposphere and transported into the stratosphere. This is explicitly stated by Hurst et al. (1999):
“The quantity P_{H_2O}/L_{CH_4} is often erroneously referred to as the “yield” of H_20 from CH_4 oxidation, even though it includes significant H_20 production from H_2 oxidation. Since $> 95\%$ of H_2 present in the lower stratosphere originated in the troposphere, the oxidation of H_2 produced by stratospheric CH_4 oxidation (1)–(5a) represents $< 5\%$ of L_{H_2}. Hence it is not possible to directly determine a true yield of H_2O from CH_4 oxidation using observations of H_2O and CH_4, and the slope of the correlation between H_2O and CH_4 ($\Delta H_2O/\Delta CH_4$) is simply P_{H_2O}/L_{CH_4}.”
We examine the contribution by CH_4 oxidation and how it can potentially be represented in CCMs. In particular, if one wants to apply a paramterization like: $\frac{d}{dt}[H_2O] = \gamma_{H_2O} \cdot \frac{d}{dt}[CH_4]$, one must be aware not to mix γ_{H_2O} with the yield from the oxidation of H_2, originating from the troposphere. We added a note to stress this on page 3.

Old: In the EMAC model (Jöckel et al., 2010), for example, explicitly configured in a CTM-like set-up without interactive chemistry, the production of SWV from CH_4 oxidation is calculated in a simplified way using a specifically introduced CH_4 tracer (by applying the CH4 submodel) according to:

$$\frac{d}{dt}[H_2O] = -\gamma_{H_2O} \cdot \frac{d}{dt}[CH_4] \tag{1}$$

with $\gamma_{H_2O} = 2$ as the yield of H_2O.

New: In the EMAC model (Jöckel et al., 2010), for example, explicitly configured in a CTM-like set-up without interactive chemistry, the production of SWV from CH_4 oxidation is calculated in a simplified way using a specifically introduced CH_4 tracer (by applying the CH4 submodel) according to:

$$\frac{d}{dt}[H_2O] = -\gamma_{H_2O} \cdot \frac{d}{dt}[CH_4] \tag{2}$$

with $\gamma_{H_2O} = 2$ as the yield of H_2O. Note, that if one wants to apply such a parameterization, one must specifically be aware not to mix γ_{H_2O} with the yield from the oxidation of H_2, originating from the troposphere.

The reason the assumption is good in the lower stratosphere, even though the calculated yield there is less than 2, is that the lifetime of CH4 there is very long (100 years). Almost all of the oxidation of methane in the stratosphere is occurring in the mid-stratosphere, where the yield is 2. This air is transported down into the lower stratosphere, so the yield in the lower stratosphere just reflects mid-stratosphere photochemistry.
This needs to be clearly laid out in the paper. Otherwise, readers will be misinformed.

We agree on the lifetime. However, we do not see a downward transport of air in the tropical stratosphere for which we present our analysis. In contrast, the BDC transports air upward in that region (otherwise no tape recorder (Mote, 1995) would be visible).

Assessing the quality of the assumption that dH2O/dCH4 = 2 would require a different analysis. All one would have to do is show regressions of H2O versus CH4 in various regions of the stratosphere (from either observations or models with full stratospheric chemistry). This comparison would show you if that assumption is good.

This is the method usually applied to observations. However, as discussed above and in our manuscript, by using the correlations of H_2O and CH_4 alone, it is not possible to distinguish between H_2O from CH_4 oxidation, H_2O from oxidized H_2, which is produced in the troposphere and transported to the stratosphere.

In fact, the paper is really about H photochemistry, not the assumption that dH2O/dCH4 = 2. There's a lot of discussion in the paper that revolves around the details of stratospheric photochemistry. So one possible suggestion that I think would improve the paper would be to remove the present motivation of the paper (testing if dH2O/dCH4 = 2) and replace it with a more accurate characterization of the work described (investigating H photochemistry and sensitivities).

Following our comment above, we are interested in the contribution of methane oxidation to SWV and how it is (or could be) represented in GCMs without a full photochemical mechanism. For this, γ_{H_2O} is required, because we need to distinguish the above indicated contributions. In order to derive this γ_{H_2O}, we apply a CCM (i.e. with detailed photochemistry) as a reference because the simple tracer-tracer correlation method cannot provide the γ_{H_2O} as we define it in our introduction (pages: 6–8).

Smaller comments

1) I would eliminate Fig. 1 below 100 hPa. This region is not relevant to the paper.

We are hesitating to cut the figures below 100 hPa for mainly two reasons: (1) the gradient accross the tropopause would not be visible anymore and (2) the consistently calculated tropopheric yield values, although not discussed, still provide valid information and serve as a reference for similar follow up studies.

2) Why do the authors spend so much time looking at OH sensitivity? That section should be motivated better.

Thank you for this suggestion. We invested some more sentences on the motivation of this section.

Old: The results of the previous section revealed that the effective yield of water vapor from CH_4 oxidation depends on the box location, hence the chemical regime at a certain pressure level. Particularly, OH is one of the major oxidants that largely controls the conversion of CH_4 to H_2 and H_2O respectively.

In the simulations shown above (Exp1) the OH is unconstrained, however, its final (equilibrated) OH concentration does not deviate much from the initial values (see Fig. 5).

New: The results of the previous section reveal that the effective yield of water vapor from CH_4 oxidation depends on the box location, hence the chemical regime at a certain pressure level. Particularly, OH is one of the major oxidants shaping the chemical regime and largely controls the conversion of CH_4 to H_2 and H_2O, respectively. In the simulations shown above (Exp1) the OH is unconstrained, however, its final (equilibrated) OH concentration does not deviate much from the initial values (see Fig. 5). The following sensitivity study aims towards understanding the relationship between the OH and the vertical profile of the yield. It is investigated whether the variations of the yield are directly related to OH variations or to other parameters.

3) I don't understand why the direct and effective yields of water vapor in the lower stratosphere are equal. The direct yield is the water vapor produced directly from methane oxidation. However, there's also a contribution from oxidation of H2 (lifetimes of CH4 and H2 are similar in the lower strat.). That would be included in the effective yield. Thus, the effective yield should be larger than the direct yield, right? I'm confused.

The direct yield indicates the water produced by methane oxidation on a direct pathway. Once water is produced, it also gets reduced and subsequently recycled. Precisely, an H atom, which was part of CH_4, migrates to H_2O and further to some H-carrying species and potentially back to H_2O. The ultimate amount of H_2O per oxidized CH_4 is the effective yield, i.e., just that part, on an equilibrated level, which stays in H_2O. The effective yield is therefore always smaller than or equal to the direct yield.
This cycle is sketched in Fig. 1. The arrows of L_{CH_4} and $P^I_{H_2O}$ are indicating the direct yield and all arrows together the effective yield. We add this information to the caption in the revised manuscript.
The contribution of H_2 is in our case only considered, if – and only if – the H_2 was previously produced by CH_4 oxidation. Recall that by applying MECCA-TAG we are able to distinguish between H introduced into the system by CH_4 from that introduced by other species.
Direct and effective yield are equal, as long as the loss of H_2O is negligible or the recycling is lossless. To avoid confusion, we added this sentence to the text of the yield definitions in the manuscript.

4) This emphasizes that I don't particularly understand the way the authors have defined effective and direct yield. It seems to me that direct yield should be production of water directly from methane oxidation and effective yield should be the direct production plus the yield of water vapor from H2 oxidation and minus the loss of H2O from photochemistry. Is this how they view their definitions? If so, they should perhaps re-phrase that part of the manuscript.

We hope that the answer above gave some additional explanation to the definition of direct and effective yield. Additional to that, we would like to stress here that the effective yield is not the sum of the direct production of H_2O from CH_4 oxidation and H_2 oxidation minus the loss of H_2O from photochemistry. We track the H atoms, which all have in common that their source is (only) CH_4. These H atoms can temporarily be part of H_2, but we are not counting oxidation of H_2 which is produced in the troposphere and transported into the stratosphere. However, we are accounting for hydrogen, which has been part of CH_4 produced H_2O, and has been recycled. The method takes care that no double counting takes place. We added some corresponding notes to the introduction of the method.

Old: In this particular case, we count the H_2O molecules created from CH_4 oxidation pathways and are able to distinguish the H from CH_4 from the H of other sources (H_2, NMHCs, HCFCs etc.). However, those that further break down to other HOx ($OH+HO_2$) compounds (and subsequently produce H_2O again) are counted separately. Overall, such an approach is the "online" approximation of the technique used by Lehmann (2004) and helps to avoid double-counting issues in yield derivation. Ultimately, we are able to quantify the fraction of H atoms populating the species of the complete ($CH_4 \rightarrow H_2O/H_2 \leftrightarrow HO_x$)-cycle, including their fractions recycled via H_2O.

New: In this particular case, we count the H_2O molecules created from CH_4 oxidation pathways and are able to distinguish the H from CH_4 from the H of other sources (H_2, NMHCs, HCFCs, etc.). More specifically, we track the H atoms, which all have in common that their source is only CH_4. These H atoms can temporarily be part of H_2, but we are not counting oxidation of H_2, which is produced in the troposphere and transported into the stratosphere. However, we are accounting for hydrogen, which has been part of CH_4 produced H_2O, and which becomes recycled after depletion of H_2O. Hence, that part of CH_4 produced H_2O, which breaks down to other HOx ($OH+HO_2$) compounds (and subsequently produces H_2O again) is counted separately. Overall, such an approach is the "online" approximation of the technique used by Lehmann (2004) and helps to avoid double-counting issues in yield derivation. Ultimately, we are able to quantify the fraction of H atoms populating the species of the complete ($CH_4 \rightarrow H_2O/H_2 \leftrightarrow HO_x$)-cycle, including their fractions recycled via H_2O.

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