Answer to the referee # 2

April 27, 2018

Dear referee,
thank you for the positive review and valuable comments on our manuscript. We address them point-by-point below. The indicated pages of the answers relate to the discussion paper.

Major comments

One I idea I had around improving the manuscript, is that the authors encourage the use of comprehensive parametrizations in GCMs – but I am not clear on what exactly these parametrizations should be? I wondered if it could be worth adding a subsection near the end called recommendations for GCMs without online chemistry, or similar.

This is a very good idea. We moved some parts concerning this into a corresponding subsection at the end of the discussion and included some additional suggestions for parameterizations. Unfortunately, we can not be very specific, since we have not yet tested the suitability of our recommendations. This will certainly be addressed in subsequent studies.

Added text on page 24:
Nevertheless, one could start with a parameterization as introduced by Eq. (1), however, with a pressure dependent $\gamma_{H_2O}(p)$ derived from our vertical yield profiles. This adds a vertical dependency to the chemical production of H_2O per CH_4 oxidized. As long as no large variations or trends in the stratospheric transport are expected within the simulation period, our profile is a good approximation. The limitation is, however, that the pressure dependence is likely to change with changing climate.

At higher altitudes (above 0.2 hPa) the yield in Eq. (1) could be replaced or supplemented by an explicit parameterization of the chemical loss of H_2O, mostly via photolysis and the reaction with $O(^1D)$, see MacKenzie and Harwood (2004) and McCormack et al. (2008). In the simplified methane chemistry of EMAC, for example, a predefined $O(^1D)$ is also used for the reaction with CH_4 and could be reused for the reaction with H_2O. Again, the same limitation holds: under climate change, water vapour, and photolysis rates are likely to change.

Im also aware of more recent parametrizations for methane oxidation, e.g. as discussed in Oman et al. (2008), whereby the rate of methane oxidation takes into account pressure, latitude and age-of-air. I think that discussing these more recent parametrizations would round out the discussion nicely.

Thank you for the note on the paper of Oman et al. (2008). Indeed, they use a paramterization (based on Austin et al (2007)) of the loss of CH_4 ($\frac{d}{dt}[CH_4]$). Note that we evaluate the yield of H_2O per oxidized CH_4, i.e. γ_{H_2O}. Both are in the parameterization of the H_2O production independent of each other:

$$\frac{d}{dt}[H_2O] = -\gamma_{H_2O} \cdot \frac{d}{dt}[CH_4] \; .$$

Austin et al. (2007) and Oman et al. (2008) still assume a yield of two H_2O molecules per oxidized CH_4. For this reason, the study of Austin et al. (2007) is mentioned in the introduction of our manuscript. A similar parameterization is for example introduced by Monge-Sanz et al. (2013).

We are hesitating to expand the discussion of the yield towards the discussion of the parameterization of the loss of CH_4 ($\frac{d}{dt}[CH_4]$), since this can be chosen individually and independent of the assumptions concerning the yield.
Our concern is further that the mentioned parameterizations do not consider the loss of H_2O, which is indeed mentioned by Oman et al. (2007) as well. There are, however, rather recent parameterizations of MacKenzie and Harwood (2004) and McCormack et al. (2008), which include the loss of H_2O applied in 2-D models and are already part of the discussion (Page 24, line 4).
Nevertheless, we added a reference to Oman et al. (2008) in the introduction, since it fits to the other mentioned papers (Monge-Sanz et al., 2013; ECMWF, 2007; Austin et al., 2007; Boville et al., 2001; Mote, 1995; Eichinger et al., 2015) using the assumption of a constant yield of 2.

Minor comments

The paper will benefit from copy editing for English, and the authors might want to find a native English speaker or two to help with that when they resubmit the final version.

Thank you for this suggestion. Please note that copy editing for language is in any case applied by the journals editorial office before final publication.

P1L18: how about at polar latitudes?

During the polar night, due to the virtual absence of OH, the method is not applicable. This is discussed in the paper. We added a sentence in the abstract as well.

Abstract:

Old: It is found in the global approach that presented results are mostly valid for mid latitudes as well.

New: It is found in the global approach that presented results are mostly valid for mid latitudes as well. During the polar night the method is not directly applicable.

P3L20: I guess you mean its not vertically well mixed, c.f. zonally.

Yes, indeed, the vertical mixing is of most concern here.

page 3:

Old: As an additional remark, it should be noted that difficulties with yield estimates can be expected especially in the stratosphere, as it is not as well mixed as the turbulent troposphere.

New: As an additional remark, it should be noted that difficulties with yield estimates can be expected especially in the stratosphere, as it is vertically not as well mixed as the turbulent troposphere.

P3L25: please state what sort of model you use in (3).

Thank you, that is indeed not clear here. We added a corresponding note.

page 3:

Old: For the third approach (3), we rely on the assumption that the hydrogen budget in the stratosphere is conserved, mostly consisting of fractions of H, H2, H2O and CH4.

New: For the third approach (3) we again use the model results of a global simulation with EMAC. This approach relies on the assumption that the hydrogen budget in the stratosphere is conserved, mostly consisting of fractions of H, H2, H2O and CH4.

P3L27 and elsewhere: note the correct spelling of explicitly.

Thank you for pointing this out. We corrected it throughout the manuscript.

P3L28-30: it wasnt clear to me what you mean by this sentence.

We want to state that the study of Johnston and Kinnison (1998) is an additional example for estimating the yield of methane oxidation. This yield is the impact of CH4 on ozone instead of H2O. We reformulated the sentence to be more concise.

page 3:

Old: Despite that this study focuses on the tropospheric and lower stratospheric ozone (O3), it is a practical example on the derivation of atmospheric trace gas yields.

New: The study of Johnston and Kinnison (1998) is an example for estimating a yield from CH4 oxidation, although it focuses on CH4 impacts on ozone (O3) instead of H2O.

P4L24: can you list the simulated intermediates here (if practical)?

Yes, we added two examples of the additional species.

page 4:

Old: The mechanism is extended to resolve specific intermediates in the CH4 → H2O reaction chain, resulting in slightly more comprehensive chemical kinetics.

New: The mechanism is extended to resolve specific intermediates in the CH4 → H2O reaction chain (e.g. methyl (CH3) and methoxy radical (CH3O)), resulting in slightly more comprehensive chemical kinetics.

P4L30: please define acronyms, e.g. NMHCs, HCFCs

Yes, of course. We added the definitions.

P4L30: how do you define HOx? H+OH+HO2?

We define HOx as the sum of OH and HO2, which is now also indicated in the text as well.

P5: Please also define NOx, ClOx and BrOx

That is included now as well.

P5L28: Id like to know more about your RC1SD-base-10 EMAC simulation. E.g., from the name, can it be inferred that dynamics are specified to a reanalysis?

Yes, that is right. SD stands for specified dynamics. We added some more information on this simulation.

This simulation is carried out at T42L90MA resolution with specified dynamics, hence a Newtonian relaxation is performed with respect to meteorological reference data (ERA-Interim reanalysis data from ECMWF (Dee et al., 2011) to be more precise) concerning the prognostic variables divergence, vorticity, temperature and (logarithm of) surface pressure.

Fig.2: where is H2O being lost to in the mesosphere?

The reduction of H2O occurs in the model due to two chemical reactions and photolysis, as indicated by Reactions (R7-R9). We added a reference in the text to make this clear.

In the mesosphere the loss of H2O especially via Reactions (R7) and (R9) increases (also evident in Fig. 2).

Table 2: the authors might want to consider adding an extra column stating whether the simulation is a box model or CCM simulation.

That is a good idea. We added such a column.

P15L21-23: Can you comment on what in particular is important regarding chemical composition of the box?

The variations are mostly dependent on the abundances of the atmospheric radicals (OH, HO2) and on the (additional) reaction partners of CH_4 ($O(^1D)$ and Cl). We added such an explanation.

page 15:

Old: Consideration of the obvious vertical dependence and the very low temperature dependence gives evidence that not the physical parameters (temperature and pressure) itself are crucial for the H_2O yield, but rather the chemical composition of the box. This chemical composition, however, changes with altitude (hence with pressure) and depends additionally on transport

New: Consideration of the obvious vertical dependence and the very low temperature dependence gives evidence that not the physical parameters (temperature and pressure) themselves are crucial for the H_2O yield, but rather the chemical composition of the box (i.e., among others, abundances of OH, HO_2, $O(^1D)$ and Cl). This chemical composition, however, changes with altitude (hence with pressure) and depends additionally on transport.

P24L13: I think its now fairly well recognised that online chemistry is necessary in many respects, e.g. the Southern Hemisphere circulation response to CO2 via O3 changes (Chiodo and Polvani, 2017).

We thank the referee for this comment. We added a note and the citation to relate our argument to the current scientific knowledge.

page 24:

Old: This raises the question, whether a simplified parameterization of γ_{H_2O} is indeed applicable for future climate projections or if it is necessary to simulate the full-chemistry, if an accurate SWV is desired.

New: This raises the question, whether a simplified parameterization of γ_{H_2O} is indeed applicable for future climate projections, or if it is necessary to simulate the full-chemistry for an accurate representation of SWV. The need of on-line chemistry for meaningful climate projections has anyway already been shown e.g. by Chiodo and Polvani (2017) for a realistic response of SH circulation to CO_2 changes.