Reply to referee # 1

October 26, 2020

Dear Referee #1,

thank you for your constructive comments on the manuscript. We appreciate your eye for detail. In the following we reply to your comments point-by-point. The indicated pages of the answers relate to the discussion paper.

1 Specific comments

I don't feel that the diagrams, particularly Figure 1 and S1, are sufficiently clear enough to represent the mechanism or equations in use, and these should be included instead, or references supplied.

Thank you for this suggestion. Initially, we decided to reduce the manuscript by omitting the chemical reactions included in the submodel CH4, as they are cited in nearly every publication concerning methane (CH_4), and provided the differential equation in form of Eq. (1) instead. However, we understand that this reduces the comprehensibility of the concept and therefore include the sink reactions of CH_4 in the revised manuscript and move the differential equation to the introduction section of the CH4 submodel.

The paper describes a submodel already somewhat extensively described by Eichinger et al, 2015a, reference in this paper, and this does potentially diminish its novelty. I think it would be important to add a clear section on any differences between the implementation described here and that already in Eichinger et al.

Thank you for pointing this out. It is true that Eichinger et al, 2015a used a preliminary version of the CH4 submodel. Since then the submodel was updated and extended by the age and emission classes and by the treatment of the four most abundant isotopologues (while Eichinger et al, 2015a included deuterated methane (CH_3D) only). In the revised manuscript, we mention these unpublished developments in the introduction. Since this manuscript in GMD is meant to be a documentation of the submodel, we think it is adequate to document all features, even if some have already been described and used by Eichinger et al. (2015), yet without a full documentation.

Included paragraph in section 1:
"An early version of the simplified CH_4 chemistry (CH4) submodel has been described by Eichinger et al. (2015). The present version has been updated and extended by the additional features for simulating age and emission classes and isotopologues."

I feel the paper would be strengthened, and the assessment of the submodel for SWV simulations improved, if a further section were added on this point. I appreciate that this is difficult given the underpinning model biases, but I would suggest, in particular, that the use of instantaneous production of 2 water molecules per CH4 oxidised might be assessed further, and it may also be interesting to ask, What is the impact of the use of the CH4 submodel on radiative forcing from all relevant species, that is H2O, CH4 and O3 vs a model in which the effect of CH4 on SWV was excluded?

Yes, this is an important point. We have studied the water vapor yield of CH_4 oxidation in detail, see Frank et al. (2018) (see also the added text in a comment below). If the CH4 submodel is used alone, there is no detailed chemical mechanism solved. Thus, in these cases there is no impact on ozone (O_3). Usually for such model setups a precalculated O_3 time series or climatology is prescribed for the radiation calculation. An evaluation of the impact of the CH_4 oxidation on the radiative forcing (with or without the impact on O_3) would be a study by itself and is clearly beyond the scope of the current manuscript, which is meant as a documentation of the submodel. Instead we refer to Revell et al. (2016), who quantified the impact of CH_4 oxidation on stratospheric water vapor (SWV), Stenke and Grewe (2005), who investigated the effect of SWV trends on stratospheric O_3 chemistry and Solomon et al. (2010), who linked changes in SWV (in particular in the upper stratosphere, where CH_4 oxidation makes the biggest impact) to global warming.

I think the paper would be improved by the addition of more detail on the impact of the choices made, particularly considering the processes or feedbacks that it was necessary to omit or treat at a reduced level of detail in the submodel and how these choices impact model skill.

Thank you for this suggestion. We decided to include a discussion why the present framework of a reduced chemistry is applicable to CH_4 and which requirements have to be met so that the simulated results are meaningful.

Included paragraph in section 3:
The presented framework of the reduced CH_4 chemistry is applicable, since CH_4 is only reduced and not produced in the free atmosphere. Therefore the discretization of the four reactions, where CH_4 is involved, is sufficient to represent the chemical loss of CH_4. Nevertheless, in order to have consistent simulation results with the CH4 submodel some prerequisites have to be met. Since the educts (the hydroxyl radical (OH), chlorine (Cl) and excited oxygen ($O(^1D)$)) are prescribed, there is no feedback on them. Thus, very large variations in CH_4 mixing ratio, which would in reality influence the CH_4 sink (Winterstein et al., 2019), are not representable by the CH4 submodel. That means it is necessary to have a balanced CH_4 mixing ratio and CH_4 sink for a sufficient simulation skill.

Assessment of the correctness of the implementation of the atmospheric feedbacks is important here, and it is unfortunate that the concept of feedback is used somewhat broadly, which slightly obstructs the reader's own assessment of what the feedbacks are between or how they arise and whether they are implemented correctly. A key feedback is that of CH4 on OH, yet the specific examples do not mention OH, or the generation of species which could be the sink for OH, such as CO. Mention is made of HO2, however.
Similarly, the use of the phrase 'predefined fields' could be made more explicit to indicate the coupling.
L7: Is the oxidation always 'offline', that is the loss of OH is not returned to the chemical solver as a feedback.

Thank you for pointing this out. We see that there is need to make the phrase 'predefined fields' more clear and when we include feedbacks and when not. 'Predefined' means that they are prescribed from outside of the CH4 submodel. The CH4 submodel does not change the sink by OH (or the other sink reactants). This explains that there are no feedbacks of the CH4 submodel on the CH_4 sink educts and why we omitted the chemical processes forming or destroying these reactants. We added text to explain this in the manuscript (see next remark).

L131: the model can be coupled to, but what is the nature of the coupling? One-way(submodel receives oxidant fields) or two-way (submodel returns depleted OH, Cl fields to MECCA)?

The coupling with the Module Efficiently Calculating the Chemistry of the Atmosphere (MECCA) is one way only, as the reactant fields defined by MECCA are imported into the CH4 submodel. The CH4 submodel does not alter the reactant fields (OH, Cl and $O(^1D)$), but it optionally does alter the water vapor. We added this explanation in the manuscript.

The prescribed fields are taken either from existing simulation results with detailed chemistry, or from other data sources (e.g. reanalyses or projections). If CH4 is included in an ECHAM/MESSy Atmospheric Chemistry (EMAC) chemistry-climate model (CCM) simulation (which is possible in the Modular Earth Submodel System (MESSy) framework), the CH4 submodel can also be coupled to the reactant fields, which are on-line calculated during the same simulation by the chemical mechanism (i.e. MECCA). Although this does not save computational requirements, such a simulation configuration can be used, for example, if output of one of the additional options of the CH4 submodel (age and emission classes or isotopologues) are desired. In that case a second CH_4 tracer is treated and oxidized by the reactants solved from the kinetic solver of the comprehensive chemical mechanism. The same applies for the photolysis rate of CH_4, which can be prescribed from offline provided gridded data or on-line calculated by the submodel JVAL (Sander et al., 2014). **In either case, the CH4 submodel does not alter the reactant fields. Hence there is no feedback on the CH_4 sink by the submodel. In case of a coupling to MECCA via the reactant fields the coupling is one-way only.**

L 138: 'secondary feedback': implies that there is feedback, but of which species?

MECCA describes the full chemical mechanism, which includes the production and loss of the reactant species OH, Cl and $O(^1D)$. We rephrase this paragraph to emphasize the difference between MECCA and the CH4 submodel.

Old:

Figure 1 visualizes the conceptual differences between the MESSy submodel CH4 (left) and a CCM simulation with MECCA (right). MECCA simulates the entire chemical mechanism and therefore also includes the feedback onto the reaction partners (depicted in yellow) of CH_4. Additionally, there is also a secondary feedback by the products from the CH_4 sink reactions (e. g. water vapour (H_2O), HO_2, depicted in blue). Conversely, the CH4 submodel uses the predefined fields of the reactant species to calculate the CH_4 loss. This loss is included in the master tracer of the CH4 submodel, but does not feedback onto the sink fields or any other chemical species, except H_2O, in the case when the hydrological feedback of CH_4 oxidation is switched on. General Circulation Models (GCMs) include CH_4 foremost for its radiative impact as a greenhouse gas, but also for its influence on stratospheric water vapor (SWV, e.g. Monge-Sanz et al. (2013); ECMWF (2007); Austin et al. (2007); Boville et al. (2001); Mote (1995)). The CH4 submodel is likewise equipped with an optional feedback onto H_2O, to account for the secondary climate feedback of CH_4. It is thereby assumed that two molecules of H_2O are produced per oxidized CH_4 molecule (le Texier et al., 1988), which is, however, only a rough approximation as analyzed by Frank et al. (2018).

New:

Figure 1 visualizes the conceptual differences between the MESSy submodel CH4 (left) and a CCM simulation with MECCA (right). MECCA simulates the entire chemical mechanism and therefore also includes the feedback onto the reaction partners (depicted in yellow) of CH_4. Additionally, there is also a secondary feedback by the products from the CH_4 sink reactions (e.g., H_2O, HO_2, depicted in blue), as the subsequent chemical processes are influenced by the products from the CH_4 oxidation. Conversely, the CH4 submodel uses the prescribed fields of the reactant species to calculate the CH_4 loss. This loss is included in the master tracer of the CH4 submodel (the present CH_4 is reduced), but does not feedback onto the sink fields or any other chemical species. The only exception is H_2O, in the case when the hydrological feedback of CH_4 oxidation is switched on. GCMs include CH_4 foremost for its radiative impact as a greenhouse gas, but also for its influence on stratospheric water vapor (SWV, e.g. Monge-Sanz et al. (2013); ECMWF (2007); Austin et al. (2007); Boville et al. (2001); Mote (1995)). The CH4 submodel is likewise equipped with an optional feedback onto H_2O, to account for part of the secondary climate feedback of CH_4. It is thereby assumed that two molecules of H_2O are produced per oxidized CH_4 molecule (le Texier et al., 1988), which is, however, only a rough approximation as analyzed by Frank et al. (2018). The approximation of two molecules H_2O per oxidized CH_4 molecule overestimates the

H_2O production in the lower stratosphere and underestimates the production in the upper stratosphere. It also does not account for the chemical loss of H_2O in the mesosphere.

Figure 1: what do the green and black lines signify? What is the meaning of the differently shaded arrows? What is the meaning of yellow and red species?

We reduced to some extent the different coloring in the figure as it has no meaning. The red species is the core species CH_4. We depicted the sink reactants in yellow. Blue is reserved for the products of the oxidation of CH_4 (H_2O only, in case of the CH4 submodel).

Figure 1: caption has what I believe should be in the text 'predefined fields without feedback' but what about the effect of HO2 on OH?

In the CH4 submodel there is no feedback of HO2 on OH. In MECCA such feedbacks are included. We changed the caption to make this more clear.

L145: Would it be possible to add what the effect of this approximation is?

Yes, we added a sentence describing the most important aspects of this approximation.

Included:
The constant approximation of two molecules H_2O per oxidized CH_4 molecule overestimates the H_2O production in the lower stratosphere and underestimates the production in the upper stratosphere. It also does not account for the chemical loss of H_2O in the mesosphere.

Does H2O feedback on stratospheric ozone?

In the case of a simulation, where the CH4 submodel is the only component simulating the atmospheric chemistry, there is no feedback of H_2O on O_3, since there is no interactively calculated O_3 tracer (usually only a prescribed O_3 climatology is used).

2 Detailed comments

L13: what does 'similar to' mean here more precisely? **We used 'similar' to point out the technical similarity in adding the produced H_2O and deuterated water vapour (HDO).**

What do you mean by 'feedback' to the isotopological hydrological do you mean 'is passed back'? **Thank you for this paraphrase as it is exactly what we mean. We changed it accordingly.**

L43: remove comma between both, natural **Agreed.**

L46: what do you mean by 'not sufficiently accurate' here? Do you mean the lifetime is too short? **Our intention is to state that the lifetime - or strictly speaking OH - is an important factor for the atmospheric chemistry, however challenging to simulate accurately. We rephrased this to: The lifetime of CH_4 is in the order of magnitude of 10 years, but its exact values is still unknown and subject to uncertainties. However, CH_4 is an important precursor of the Ox/HOx chemistry in CCMs. For this reason, in most CCM setups CH_4 is prescribed at the lower model boundary to achieve a realistic CH_4 burden independent of the simulated lifetime.**

L56: reference required? **We revised the given values and added a reference.**

L60: Earth's surface **Agreed.**

L74 *and* L80: rate constant not rate, given what comes after in the text, k is usually reserved for rate constant but this is of course correct **Thank you for pointing this out. Although we decided to change the term to rate coefficient, since it is not constant. We removed this confusion of notation here and in the whole manuscript.**

L114: insert 'to' so as will read 'submodel to represent' **Agreed.**

L186: modify 'is not conform with' *and* **L193:** modify 'to be conform with' **We corrected *conform* by *consistent.***

L200: drop comma between 'choose, whether' **Agreed.**

L220: would make more sense as a list: 1) the CH4 submodel, 2) MECCA_TAG and 3) H2O... **Agreed.**

L221-222: drop 'are treating' **We changed this to *include.***

L231: 'doubles' is not very clear: do you mean 'duplicates'? **Thank you, we adopted this suggestion.**

L303: replace 'most and largest' with 'most importantly'? **We reduced it to "Most isotopically light emissions...", since we refer to the magnitude and extent of the emission.**

L306: sentence is rather inelegant. **We revised this to: "When CH_4 is ascending in the atmosphere it is exposed to oxidation. Due to fractionation processes heavy CH_4 isotopologues are unfavored and therefore accumulate in the remaining CH_4 content."**

L308-317: values are required for quantitative comparison. **We added more concrete results in the supplement.**

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