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Response to Editor

Dear Mr Morgenstern,

According to the reviews, we thoroughly revised the manuscript "An advanced method of contributing emissions to short-lived chemical species (OH and HO_2): The TAGGING 1.1 submodel based on the Modular Earth Submodel System (MESSy 2.53)". We restructered the manuscript and set the case "tag" as baseline of the manuscript. We moved the discussion about omitted reactions in the appendix. Moreover, we merged the Section "Steady-state assumption" and "Closure of the budget" and we better justified the introduction of the rest terms. We also intensively modified the representation of the results.
We think that the manuscript gained readability and clarity. We hope that we have satisfactorily addressed all comments of the reviewers.

Yours sincerely,

Vanessa Rieger

Attachments:

- Response to Reviewer #1
- Response to Reviewer #2
- List of relevant changes
- Marked-up manuscript

Response to Reviewer #1

We would like to thank the reviewer for thoroughly examining the manuscript. We gratefully incorporated the reviewer's comments which certainly improved our manuscript. Please find below our replies in italics and indented.

General comments

The present study by Rieger et al. presents an updated tagging algorithm for OH and HO2 which allows for an attribution of HOx to various emission categories. In contrast to the previous version V1.0 the new version takes into account tropospheric as well as stratospheric chemistry. Furthermore, the new scheme considers rest terms to take into account HOx production and loss reactions which are not explicitly tagged.

Since the tagging mechanism does not only consider primary contributions, but also secondary effects via the long-lived species, the paper is rather difficult to read. I am sure for the authors, who are familiar with the tagging approach, it is clear what's going on, but for an unacquainted reader it is difficult to understand why an updated tagging method for HOx results in different contributions of, e.g., biomass burning emissions to ozone. Maybe a schematic would be helpful. Furthermore, the HOx tagging includes several assumptions and special cases. There are several open questions (details see below). My major concern is related to the steady-state assumption and the rest terms. Overall, I think the paper needs a clearer description of the method, a better justification of the assumptions and a more thoroughly explanation of the presented results.

> *We added some further explanation in the introduction about the interaction between short-lived and long-lived species to clarify the relations. As suggested by the reviewers, we also inserted a sketch explaining the interaction between long-lived and short-lived species (Fig. 1). We also restructured the manuscript by merging Section "Steady-state assumption" and "Closure of the budget". We further set the case "tag" as baseline for the manuscript as was suggested by reviewer #2. Moreover, we better justified the introduction of the rest terms in Sect. 3.4. We also tried to present the results in a better and more understandable way. We hope that this improves readability of the manuscript. Details of the changes are described below.*

In the introduction the authors argue that mitigation of climate change requires attribution of certain chemical trace gases to specific emission categories, and therefore propose the tagging approach. I wonder how robust the presented results are. For example, the presented model simulations do not consider direct CH4 emissions. I assume that tagging CH4 from the applied emission categories would have a large impact on the attribution of HOx to certain emissions. In my opinion it is inconsistent to consider CH4 decomposition as one category, while NOx, NMHCs etc. are split into road traffic, non-traffic etc. For an evaluation of the overall climate impact all traffic related emissions have to be tagged in the same manner. Therefore, I have doubts that the method is already applicable.

> *This is a good point. Indeed, it would be desirable to also tag CH_4. However, for the current state-of-the-art, this is not possible. Estimates of CH_4 lifetime are still quite uncertain. In particular, CH_4 lifetime against OH is generally underestimated by chemistry climate models (Jöckel et al., 2016). But CH_4 is an important greenhouse gas. Thus, to hold CH_4 lifetime on a reasonable level, CH_4 emissions are generally prescribed in state-of-the-art chemistry climate models. Therefore, considering the current treatment of CH_4 in chemistry climate model, it is not reasonable to tag CH_4.*

> *Considering the tagging of CH_4 would of course change these categories where CH_4 emissions play a role. However, for those categories where CH_4 emissions do not play a major role, no large changes are expected. For example, for road traffic and shipping emissions, direct CH_4 emissions are not important. Consequently, no large changes are expected if the tagging of CH_4 would be included. Hence, the current implementation of the HO_x tagging method enables to determine the contribution of traffic emissions to HO_x.*
>
> *Note that we do not expect large changes in contributions from methane decomposition since this relies on CH_4 concentrations which are reasonable due to boundary conditions. However, a part of this decomposition will be allocated to other sources.*

In the first sentence of Sect. 3.3 the authors state it is crucial that HOx production and loss of the reduced mechanism (almost) equal the complete HOx production and loss. Furthermore, steady state means to me that HOx production equals HOx loss. This is valid for the complete HOx chemistry derived from MECCA, but not or only partly for the reduced system. For example, stratospheric OH production of V1.1 deviates by 9% from the total stratospheric OH production and, maybe even more important, from the stratospheric OH loss of V1.1. Therefore, I do not agree with the conclusion at the end of section 3.3 that the steady-state assumption for the reduced reaction system V1.1 is justified. If the steady-state assumption was fulfilled, the rest terms to close the budget would be needless.

> *We agree that end of Sect.3.3 could be confusing. In fact, it referred to the reduced HO_x reaction system taking all 30 reactions into account. For this case, the steady-state is valid for tropospheric OH as well as for tropospheric and stratospheric HO_2. Indeed, for the stratospheric OH, the production and the loss deviates by 9% and thus are not in steady-state. We have rewritten the paragraph and emphasized that the steady-state assumption for the reduced HO_x reaction system V1.1 is not completely fulfilled.*
>
> ***Changes in manuscript:***
>
> *Summing up, the reduced HO_x reaction system V1.1 represents well the total HO_x production and loss in the troposphere and stratosphere. V1.1 reproduces the HO_x chemistry better than V1.0. However, OH production in troposphere and stratosphere as well as H loss in the stratosphere of V1.1 deviates from the total rates derived by MECCA. Thus, the state-state for the reduced HO_x and H reaction system (Tables 1 and 2) is not completely fulfilled.*

Furthermore, it is not clear from the paper that the steady-state assumption for H is valid, as claimed in Sect. 3.4.

> *We agree with the reviewer that we missed to explain this point. To show that steady-state of H is valid, we have added this information to Table 3 and discussed the steady-state of H in Sect. 3.4.*
>
> ***Changes in manuscript:***
>
> *The reduced H reaction system in V1.1 (Table 2) represents the total H production and loss in the troposphere very well. However in the stratosphere, H loss in V1.1 deviates by 17 % from the total H loss.*

Table 3 presents the “main reactions of H” for the reduced system, but is this reaction system identical to the complete chemical mechanism in MECCA or only a subset?

> *Table 3 shows a subset of the complete chemical mechanism in MECCA. The compete MECCA mechanism contains 15 reactions concerning H. To clarify the misunderstanding we have added an explanation in the text.*
>
> ***Changes in manuscript:***
> *Table 3 presents the main reactions for H which still constitute a subset of full H chemistry implemented in MECCA.*

Section 4 is mainly a description of the presented figures, but lacks explanations, for example for the differences between V1.0 and V1.1. The argumentation is often rather vague, namely that V1.1 considers now more reactions which contributes to the differences. That leaves the impression that the authors themselves do not fully understand the changed patterns. From what is written in the paper it is hard to understand the presented results and differences, but I think this is important to judge the performance and shortcomings of the tagging method.

> *Thank you for this comment. As you suggested we have replaced Fig. 2-4 in the manuscript by Fig. 1 and 2 from the Supplement. We agree that this makes the comparison between V1.0 and V1.1 easier.*
> *We have stated the given explanations more precisely and hope that this can clarify the presented results. For example, we have merged the examples which are based on the same explanations.*
>
> ***Changes in manuscript:***
> *The contribution of the category "aviation" to HO_2 in V1.1 shows roughly the same pattern compared to V1.0. However, the HO_2 destruction along the flight path is not as pronounced anymore which is caused by the inclusion of reaction (15) and (18) to V1.1. Reaction (15) adds the term $\frac{1}{2} R_{15}\, NO_y^i/NO_y$ to the HO_2 loss (eq. 12) and reaction (18) adds the term $R_{18}\, NO_y^i/NO_y$ to the HO_2 production (eq. 11). As reaction rate R_{15} equals the rate R_{18}, this leads to a larger HO_2 production than HO_2 loss ($R_{18}\, NO_y^i/NO_y > \frac{1}{2} R_{15}\, NO_y^i/NO_y$). Consequently, the addition of reaction (15) and (18) to the reduced HO_x reaction system V1.1 constitutes an extra HO_2 source.*
> *Larger values of the categories "N_2O decomposition" and "lightning" to HO_2 in the upper troposphere are explained by a larger HO_2 production in V1.1 compared to V1.0. The H tagging in V1.1 considers all relevant HO_2 sources (reaction (7), (10), (11) and (28)) leading to a larger HO_2 production. Also the addition of reactions (15) and (18) (explanation see above) as well as the addition of reaction (23) which considers more reactions than in V1.0 increase the HO_2 contribution of the categories "N_2O decomposition" and "lightning".*
> *Large changes in pattern are observed for the contributions of "biogenic emissions" and "CH_4 decomposition" to OH and HO_2 as well as for the contributions of "biomass burning" and "anthropogenic non-traffic" to OH. In V1.1, these categories mainly constitute a source of OH and HO_2 in the troposphere. The addition of reaction (24) and (25) to the reduced HO_x reaction system V1.1 presents a HO_2 source increasing OH and HO_2 contributions. Furthermore, reactions of NMHC with OH, HO_2 and NO_y (reaction 21, 22 and 23) are important throughout the whole troposphere. In contrast to V1.0, V1.1 considers all reactions of NMHC with OH, HO_2 and NO_y (see Sect. 3.2) significantly changing the pattern of "biogenic emissions", "CH_4 decomposition", "biomass burning" and "anthropogenic non-traffic".*

For example, what is the reason for the changes in the contribution of stratospheric O3 production to tropospheric OH?

> *Although the reactions of OH and HO_2 with $O(^3P)$ play only a minor role in the troposphere, their addition to reduced reaction system modifies the contributions to OH. Additionally, the re-establishment of the steady-state also increases the*

> *contribution of stratospheric O_3 production to OH and thus causes the change in pattern.*

Furthermore, I am concerned about the HO2 shipping contribution discussed in Fig. 6. In this case the authors provide a clear explanation, but frankly speaking this example seems to show that the tagging method does not work. Two reactions (production and loss) with the same reaction rate, but only half of the loss is considered???

> *The addition of new reactions to the reduced HO_x reaction system changes the contribution of these sectors where the new reactions are relevant. For the category shipping, all reactions concerning NO_y are relevant. Thus adding reaction (15) and (18) does change the contribution of shipping emissions to HO_2 significantly. We added further explanations in the text to clarify the change of sign due to addition of reactions (15) and (18).*
> *This example shows that in V1.0 not all relevant reactions concerning NO_y have been considered which leads to errors in the contribution calculations. In comparison, in V1.1, the tagging method overcomes these shortcomings.*
>
> ***Changes in manuscript:***
> ***Explanation:***
> *The contribution of the category "aviation" to HO_2 in V1.1 shows roughly the same pattern compared to V1.0. However, the HO_2 destruction along the flight path is not as pronounced anymore which is caused by the inclusion of reaction (15) and (18) to V1.1. Reaction (15) adds the term ½ $R_{15}\ NO_y^i/NO_y$ to the HO_2 loss (eq. 12) and reaction (18) adds the term $R_{18}\ NO_y^i/NO_y$ to the HO_2 production (eq. 11). As reaction rate R_{15} equals the rate R_{18}, this leads to a larger HO_2 production than HO_2 loss ($R_{18}\ NO_y^i/NO_y > ½\ R_{15}\ NO_y^i/NO_y$). Consequently, the addition of reaction (15) and (18) to the reduced HO_x reaction system V1.1 constitutes an extra HO_2 source.*
>
> ***Example HO_2 shipping:***
> *The change of sign is caused by the addition of reaction (15) and (18) to the reduced HO_x reaction system V1.1 which constitutes a net HO_2 production leading to positive HO_2 contributions (explanation see above). The comparison shows that HO_2 contributions in V1.0 were systematically and erroneously underestimated.*

Specific comments

- P1, L11-14: As mentioned above, at first glance it is hard to understand why the tagging of HOx affects other tagged species. If you do not want to lose your readers right at the beginning, you should consider rewriting the last part of the abstract.

> *Very good point. We definitely want to avoid losing readers already at the abstract. We added further explanations in the introduction and abstract of how the tagging of short-lived and long-lived species interacts. A detailed description of the tagging of long-lived species is found in Grewe et al. (2017).*
>
> ***Changes in manuscript:***
> ***Abstract:***
> *As HO_x reacts with ozone (O_3), carbon monoxide (CO), reactive nitrogen compounds (NO_y), non-methane hydrocarbons (NMHC) and peroxyacyl nitrates (PAN), the contributions to these species are also modified by the advanced HO_x tagging method V1.1.*
>
> ***Introduction:***

The contributions to long-lived and short-lived species are closely linked. For example, the reaction

$OH + O_3 \rightarrow HO_2 + O_2$

involves the long-lived species O_3 *and the short-lived species OH and* HO_2*. Hence, this reaction is considered in the implementation of the tagging method for long-lived and short-lived species. The contribution of, for example, shipping emissions to* O_3 *influences the contribution of shipping emissions to* HO_2*: the higher the contribution to* O_3 *is the more* HO_2 *is attributed to shipping emissions. Furthermore, OH from shipping emissions destroys* O_3 *and thus reduces the contribution of shipping emissions to* O_3*.*

- P2, L8: For which specific environments? Please clarify.

Thank you for this hint, we added an example.

Changes in manuscript:
For certain environments, such as marine boundary layer, model studies compare well with measurements.

- P4, L2/3: Why do you use a different time period for the global and the regional simulations (2007/2008 vs. 2009/2010)?

We agree that this might we confusing. Therefore, we have repeated the EMAC simulation for the same time period 2007/2008 and adjusted the plots, tables and numbers in the paper to represent the year 2008. However, we leave the dates of Fig. 6 to be able to compare it with Grewe et al. (2017).

- P5, L7/8: I am not sure if I understand this statement correctly: In V1.0 the OH loss by the reaction with NMHCs was obtained from the total chemical CO production, no matter if OH was involved or not?

Yes, this is right. The reaction rate of OH + NMHC was determined only by the net CO production. We added some further explanation to clarify the calculation of the reaction rate in V1.0.

Changes in manuscript:
The reaction rate of OH with NMHC (reaction 21, Table 1) was determined via the production rates of CO by assuming that each reaction of OH with NMHC produces one CO molecule. This method neglects all intermediate oxidation reactions of NMHC and considers only these reactions when NMHC is finally oxidized to CO.

- P5, L17/18: Reaction rates depend on the concentrations of the reactants and via the rate coefficient often on temperature, and therefore vary in time and space. So how is the threshold reaction rate of 1e-15 mol/mol/s to interpret? Is that an annual and global mean value?

Thank you, we did not mention this in the text. The threshold is a tropospheric or stratospheric annual mean. We added an explanation in the text.

Changes in manuscript:
We consider only reactions with a tropospheric or stratospheric annual mean reaction rate larger than 10^{-15} *mol* $mol^{-1}s^{-1}$ *(see Table 1).*

- P5, L21-31: What's the point of those two paragraphs? As long as you do not show any numbers, this part is rather vague.

> *Thank you for pointing this out. We added the amounts of relative contributions of the mentioned reactions to the text.*
>
> ***Changes in manuscript:***
> *The reactions which are important in the troposphere are indicated in Table 1. As stated above, reaction (1) of H and O_2 dominates the HO_2 production in the troposphere. It produces 49 % of tropospheric HO_2. In V1.0, only part of this HO_2 source was regarded (see Sect. 3.1). The most important HO_2 loss is the reaction with NO (reaction 14) followed by the reaction with itself producing H_2O_2 (reaction 3) which accounts for 32 % and 12 % of tropospheric HO_2 loss. The production via H2O and $O(^1D)$ produces about 21 % of tropospheric OH (reaction 2). The excited oxygen radical ($O(^1D)$) originates from the photolysis of O_3. Also reaction (14) of NO and HO_2 produces 32 % of tropospheric OH. OH is mostly destroyed by CO (reaction 11, 38 %) followed by NMHC (reaction 21, 25 %).*
> *In the stratosphere different chemical reactions become important. Here, OH is mainly destroyed by O_3, producing 40 % of stratospheric HO_2. The reaction is partly counteracted by the reaction (14) which produces 21 % of OH and destroys 24 % of HO_2. Since large quantities of O3 are found in the stratosphere, O_3 or the excited oxygen radical ($O(^3P)$) destroys about 62 % of HO_2. Reactions with NMHC, CO and CH_4 play only a minor role in the stratosphere.*

- P5, L33: Why are reactions 19, 28 and 30 listed in Table 1, when they are not part of V1.1? That's inconsistent with the table caption.

> *Yes indeed, there is contradicting. We have set the case "tag" as the baseline of the manuscript. Thus, Table 1 now represents only the reduced HO_x reaction system V1.1 as the table caption says. The extra information is deleted and put into the appendix A.*

- Table 1: How are NMHCs treated in the HOx tagging? Is there only one lumped NMHC or are the individual NMHCs treated separately? If it is a lumped NMHC, how often can it react with OH?

> *NMHC represents a chemical family which contains for example CH_3OH, CH_3O_2, CH_3OOH, HCHO, C_2H_6, C_2H_4 and CH_3CO_3. All species included in the chemical family NMHC are given in Table 1 in the Supplement of Grewe et al. (2017). The reaction rate of the reaction NMHC + OH → NMHC is determined by adding up all reaction rates of OH with the species of the family NMHC. We added further explanation to the text.*
> *The number of reactions with OH is an interesting point, which we haven't followed yet. But that is something we might look into in future applications.*
>
> ***Changes in manuscript:***
> *Reactions (21) to (25) involve the chemical family NMHC which contains several species such as formaldehyde (HCHO), ethylene (C_2H_4) and propane (C_3H_8). The rate for reaction (21) is determined by adding up the rates of all reactions of OH with each single species of the family NMHC.*

- Table 2: How exactly are the tropospheric and stratospheric production and loss rates calculated? I assume there is a kind of air mass weighting applied? mol/mol/s is a somehow weird unit, I would usually expect something like Tg(OH)/yr…

> *The production and loss rates indicate annual means for the tropospheric and stratospheric domain. To calculate the means, each grid box is weighted with the corresponding air mass. We added this information to the table caption.*
> *Concerning chemical reactions in the atmosphere, mol/mol/s is the usual unit for production and loss rates.*
>
> ***Changes in manuscript:***
> *Annual mean of OH, HO_2 and H production and loss rates (air mass weighted)*

- P8, L2: It is true that the OH production for "all" differs only by 2% from the total production, but for "tag" the difference is about the same as for V1.0, namely around 11%. Which quantity is used for the tagging – "all" or "tag"?

> *We agree that the discussion of the case "tag" and "all" was confusing. In the former version, the case "tag" is finally implemented in EMAC. For the current version, we set the implemented version "tag" as baseline for the paper. We hope this improves the readability of the paper.*

- P9, L25: Why are the mentioned species not explicitly tagged? Please explain.

> *This is a good point. We missed to mention it. Due to limited computational resources, it is unfortunately not possible to tag all relevant species. This is also the reason why we also tag chemical families such as NO_y and NMHC. We added an explanation in the text.*
>
> ***Changes in manuscript:***
> *Due to limited computational resources, other species such as H_2, H_2O_2, CH_4, ClO and BrO are not tagged (as in V1.0).*

- P10, L8: I do not understand this sentence. Ratio of what to what?

> *The sentence refers to the ratio A^i/A. To clarify this, we have rewritten the paragraph.*
>
> ***Changes in manuscript:***
> *In reaction (1), neither H nor O_2 are tagged. To obtain the ratio HO_2^i/HO_2, we set up an extra tagging of H itself.*

- P10, L19: Why are H2O2 production and loss not balanced? Please explain. And HOx production and loss of the V1.1 reaction system are also not balanced, but nevertheless steady-state is assumed. This is inconsistent to me.

> *H_2O_2 is not a radical, so we do not expect that production of H_2O_2 balances the loss of H_2O_2. In contrast, OH and HO_2 as well as H are all radicals which react very fast with many species in the atmosphere. Thus, steady state of OH, HO_2 and H is reached very fast. However, the reduced HO_x reaction system V1.1 is indeed not balanced. Therefore, we introduce the rest terms.*

- P11, L14: In my view this is in contradiction to the statement at the end of Sect. 3.3 (-> steady-state assumption justified).

> *We agree that the formulation at the end of Sect. 3.3 could be misleading. In the former version, end of Sect. 3.3 related to the case "all" which caused this misunderstanding. Since we now changed the manuscript and put the case "tag" as baseline of the manuscript, we modified the statements at the former end of Sect 3.3. So the introduction of the rest terms should be better justified now.*

- P11, L28/29: Why are the rest terms equally distributed amongst the source categories (division by n) and not according to the contribution of the individual source categories to the total, e.g. OHi/OH? Couldn't it be that the linear distribution of the rest terms leads to an artificial exaggeration of a minor source category? I would be interested to see the contribution of the rest terms to the individual source categories.

> *For example, a large part of the rest term for OH (resOH) originates from omitting the photolysis of H_2O_2 which produces OH. The question is now: From which source category does H_2O_2 come from? To which sector shall the produced OH attributed to? Since we don't know from which sector OH originates, we split it up equally among the sectors. Indeed, this method weights minor source categories stronger with the rest terms than major categories. However, a linear apportionment would assume that we know the origin of H_2O_2 what we indeed don't know.*
> *We provide figures showing resOH, resHO2 and resH in the supplement.*

- P14, Fig. 2: What is the reason for the different patterns in OH from anthrop. non-traffic, traffic and shipping? All three categories represent surface emissions.

> *Right, emissions of the sector anthropogenic non-traffic, road traffic and shipping are all surface emissions, but their composition and amounts are very different. For example, for the sector "anthropogenic non-traffic" CO emissions are dominating while for shipping, NO_y emissions are dominating. Consequently, these three sectors cause a different response of the atmospheric chemistry and thus also different OH patterns (e.g. Hoor et al., 2009).*
> *Moreover, shipping emissions occur over the ocean where convection is less strong than over the land. This further explains that the contributions of shipping to OH are rather confined to the lower troposphere and do not reach as high into the free troposphere.*
>
> ***Changes to manuscript:***
> *The contributions vary among these categories of surface emissions as not only the amount but also the composition of the emissions differs.*

- P16, L5/6: Please explain how the inclusion of more NMHC reactions leads to the changed pattern. In general, the treatment of NMHCs is not clear to me. Is there one lumped NMHC tracer?

> *In the detailed chemistry scheme (MECCA) species are treated individually. For the tagging scheme they are lumped and the total reaction rate is taken as a sum from the detailed scheme. Hence in the tagging method, NMHC is a chemical family and includes species such HCHO, C_2H_4 and C_3H_8. The rates of reactions including NMHC are calculated by adding up all reaction rates from each single species in the family NMHC. Consequently, a change in the reaction rate also changes OH and HO_2 contributions.*
> *We added these explanations to the manuscript.*
>
> ***Changes to manuscript:***
> *Reactions (21) to (25) involve the chemical family NMHC which contains several species such as formaldehyde (HCHO), ethylene (C_2H_4) and propane (C_3H_8). The rate for reaction (21) is determined by adding up the rates of all reactions of OH with each single species of the family NMHC.*

- P17, L2/3: How do NOy emissions contribution to the category "N2O decomposition"?

Thanks, this was unartfully expressed. Decomposition of N_2O is a source of NO_y in the stratosphere. We have thoroughly rewritten the paragraph.

Changes to manuscript:
Larger values of the categories "N_2O decomposition" and "lightning" to HO_2 in the upper troposphere are explained by a larger HO_2 production in V1.1 compared to V1.0. The H tagging in V1.1 considers all relevant HO_2 sources (reaction (7), (10), (11) and (28)) leading to a larger HO_2 production. Also the addition of reactions (15) and (18) (explanation see above) as well as the addition of reaction (23) which considers more reactions than in V1.0 increase the HO_2 contribution of the categories "N_2O decomposition" and "lightning".

- P19, L16/17: How does the HOx tagging affect stratospheric O3 production? Is it that HOx produced from ozone formed in the stratosphere leads to stratospheric ozone formation/destruction via the catalytic HOx cycles? But how would that fit with the family concept?

Ozone produced in the stratosphere does also influence the concentration of OH and HO2. O_3 reacts with OH and HO_2:
$OH + O_3 \rightarrow HO_2 + O_2$
$HO2 + O_3 \rightarrow OH + 2\ O_2$
As these reactions involve long-lived and short-lived species, they are regarded in the implementation of the tagging method for long-lived as well as in the tagging method for short-lived species.
Consequently, if the contribution of the sector "stratospheric O_3 production" to OH and HO_2 changes, this also affects the contribution to O_3.

- Conclusions: The first paragraph has a lot of redundancy and should be shortened. This holds for several parts of the manuscript. And the second paragraph is more a repetition of the abstract than real conclusions.

We have shortened the first part of the conclusion and added some further concluding thoughts.
We tried to avoid redundancy in the manuscript. However, we find it difficult to spot these redundancies because they also lead the reader through the manuscript. We tried to find a balance between redundancy and information necessary to understand the individual parts. We do not expect the reader to have read the whole manuscript, unlike the reviewer. Hence, a certain redundancy is required.

Changes to manuscript:
Please refer to the Sect. 5 Discussion and Conclusion.

- P21, L24-26: I assume that the local maximum around 5 hPa is a secondary effect via ozone?

Thank you for this comment. The photolysis of HOCl becomes important at around 5 hPa. Omitting this reaction from the tagging mechanism V1.1 leads to higher rest terms which are in turn responsible for the local maximum of HO_2 contributions at 5 hPa.
We added an explanation to the text.

Changes to manuscript:
The categories "biogenic emissions", "lightning", "biomass burning", "anthropogenic non-traffic", "road traffic", "shipping" and "aviation" show a local maximum at around 5 hPa which is caused by omitting the photolysis of HOCl (see Appendix A).

- There is no single reference to the supplement in the manuscript. So why are those additional figures shown at all in the supplement? Honestly, I would prefer to see Fig. 1 and 2 from the supplement in the main paper instead of Fig. 2 – 4. That would make the comparison of V1.0 and V1.1 easier.

> *Thank you, this is a good point. We added references to the supplement. As you recommend, we also replaced Fig. 2-4 in manuscript by Fig. 1 and 2 from the supplement to enable a better comparison of V1.1 and V1.0.*

Technical comments

- Avoid overusing the definite article, e.g. P1, L21: "HOx impacts global warming and local air quality: : :" or P2, L4: ": : :human impact on climate and air quality: : :."

> *Thank you. Where possible, we tried to avoid the usage of "the".*

- Caption Table 1, 3: "In the column "tropos." ("stratos.") reactions which are : : :."

> *Changed.*

- P7, L2: Do you mean Sect. 3.3 instead of 3.4?

> *We actually wanted to refer to points 4. and 5. in Sect. 3.4. However, since we have restructured the manuscript, this is obsolete.*

- Eqn. 5: There is a mistake. For a unimolecular reaction, there is no LossBi, rather a ProdBi. And the reaction rate is reduced to R=kA, right? Should be mentioned.

> *Thank you for the correction. We added the adjusted reaction rate.*

- Eqns. 8 and 9: Is it possible that ProdHi and LossHi are swapped?

> *Thank you. We switched the labelling.*

- Eqn. 18: I assume the third term on the right side should read -LHO2 instead of -PHO2

> *Thank you for the correction. We changed it.*

- Eqns. 23 and 24: Why are the rest terms includes in Ai and Bi? Doesn't that lead to a double-counting of the rest terms in eqn. 17 and 18?

> *Thank you for this correction. This is a mistake. As the rest term are already mentioned in eqs. (17) and (18), they must not be repeated in eq. (23) and (24). We deleted them.*

- P14, L26: "This overall shift: : :"

> *Changed.*

- P21, L22: "large negative minimum" is a rather sloppy expression, please rephrase.

> *We modified the wording.*

Changes to manuscript:
The large OH loss in the lower stratosphere

- Fig. 1: The reddish and pinkish lines are hard to distinguish, at least when printed. And I suggest to change the y-axis to 1.e-14 or 1.e-13 mol/mol/s to be consistent with the numbers given in the text.

We deleted the figure 1 from the manuscript as the basic information is contained in Table 3 where we also included the production and loss rates of H tagging.

- Caption Fig. 1: “(a) and (b) show the rates for the troposphere, : : :”

Changed.

- Caption Fig. 2, 3, 6, A1, A2: “Zonal means : : : are shown.” Simluation -> Simulation

Changed.

- Caption Fig. 4, 5: consisted -> consistent

Changed.

References:

Grewe, V., Tsati, E., Mertens, M., Frömming, C., and Jöckel, P.: Contribution of emissions to concentrations: the TAGGING 1.0 submodel based on the Modular Earth Submodel System (MESSy 2.52), Geosci. Model Dev., 10, 2615-2633, https://doi.org/10.5194/gmd-10-2615-2017, 2017.

Hoor, P., Borken-Kleefeld, J., Caro, D., Dessens, O., Endresen, O., Gauss, M., Grewe, V., Hauglustaine, D., Isaksen, I. S. A., Jöckel, P., Lelieveld, J., Myhre, G., Meijer, E., Olivie, D., Prather, M., Schnadt Poberaj, C., Shine, K. P., Staehelin, J., Tang, Q., van Aardenne, J., van Velthoven, P., and Sausen, R.: The impact of traffic emissions on atmospheric ozone and OH: results from QUANTIFY, Atmos. Chem. Phys., 9, 3113-3136, https://doi.org/10.5194/acp-9-3113-2009, 2009.

Jöckel, P., Tost, H., Pozzer, A., Kunze, M., Kirner, O., Brenninkmeijer, C. A. M., Brinkop, S., Cai, D. S., Dyroff, C., Eckstein, J., Frank, F., Garny, H., Gottschaldt, K.-D., Graf, P., Grewe, V., Kerkweg, A., Kern, B., Matthes, S., Mertens, M., Meul, S., Neumaier, M., Nützel, M., Oberländer-Hayn, S., Ruhnke, R., Runde, T., Sander, R., Scharffe, D., and Zahn, A.: Earth System Chemistry integrated Modelling (ESCiMo) with the Modular Earth Submodel System (MESSy) version 2.51, Geosci. Model Dev., 9, 1153-1200, https://doi.org/10.5194/gmd-9-1153-2016, 2016.

Response to Reviewer #2

We would like to thank the reviewer for the helpful comments on the manuscript. It helped a lot to improve our manuscript and to increase the readability. Please find below our replies in italics and indented.

1 General Comments

This paper presents an improvement to an existing and already implemented scheme, describing in detail the "tagging" of OH, HO_2, and H, by source sector. This is certainly a useful exercise. However, I found this paper confusing, as well as containing numerous errors. In its current form I am unable to recommend its publication in GMD.

> *Based on the reviewer's comments, we thoroughly revised and restructured the manuscript. We agree with the reviewer that the case "tag" as baseline is better suited and we adapted the manuscript accordingly. In addition, we modified the presented figures and put the contour levels on a common scale, as suggested by the reviewer. We think that the method and results are now represented in a better way.*

2 Specific Comments

I found the description of the tagging (Section 3.4) very confusing - the terms "explicit tagging" and "specific tagging" are used, and seem to mean different things. Longer-lived species are also tagged by source region, but the paper does not make clear the difference in this tagging and the explicit or specific tagging mentioned. It is clear that this process is complicated and requires careful consideration, but it is not explained in a way that I could easily understand. Perhaps some sort of graphical description would be helpful here?

> *Obviously the text was misleading. There is no explicit or specific tagging. There is only one tagging method which we are using. This tagging method along with different assumptions based on the lifetime of the regarded species leads to different implementations. We changed the corresponding wordings to clarify this.*
> *We added further explanations on how the tagging of the short-lived and long-lived species influence each other in the introduction. As suggested by the reviewers, we also inserted a sketch explaining the interaction between long-lived and short-lived species (Fig. 1). The implementation of the long-lived tagging is explained in detail in Grewe et al. (2017).*
>
> ***Changes in manuscript:***
> *The contributions to long-lived and short-lived species are closely linked. For example, the reaction*
> $OH + O_3 \rightarrow HO_2 + O_2$
> *involves the long-lived species O_3 and the short-lived species OH and HO_2. Hence, this reaction is considered in the implementation of the tagging method for long-lived and short-lived species. The contribution of, for example, shipping emissions to O_3 influences the contribution of shipping emissions to HO_2: the higher the contribution to O_3 is the more HO_2 is attributed to shipping emissions. Furthermore, OH from shipping emissions destroys O_3 and thus reduces the contribution of shipping emissions to O_3.*

When extending the tagging scheme to include more reactions (listed in Table 1 of the paper), reactions 19 (H_2O_2+hv->2OH), 28 (HOCl+hv->OH+Cl), and 30 (HOBr+hv->

OH+Br) are highlighted as being unable to be considered in the tagging scheme. However, the authors then include these reactions in Table 2 ("reduced - V1.1 all") and also in the line plots in Figure 1. They seem to make-up around 9% of the OH production rate, so I can see why they should be mentioned, but I was frustrated that they were given prominence over the "reduced - V1.1 tag" scheme, which is what was actually implemented in the model. Indeed, in Table 2 the OH loss and HO_2 production and loss rates are given alongside the "all" row and not the "tag", which I personally do not think is correct. I would see the "tag" scheme presented as the baseline, and the "all" is an extension to this. There is discussion in Section 3.3 about how good the "all" scheme is, but given it can't be used, why discuss it at all in this context?

> *Thank you for this recommendation. We changed the manuscript and set the case "tag", which is finally implemented in EMAC, as baseline of the manuscript. The moved the explanation about omitting certain reactions in the appendix. We hope the manuscript gained more readability.*

I was also confused about the rest terms introduced in Section 3.5. I appreciated that closing the budget is desirable, but I do not believe that the text in Section 3.5 justifies or explains their introduction sufficiently, and they seem very artificial. Can the authors please expand on this justification and the necessity for having these terms?

> *Thank you for this comment. We agree that the justification was not comprehensive. The steady-state assumption is the basic principle of the tagging method for short-lived species. As we consider a reduced HO_x reaction system, the steady-state between production and loss is not fulfilled. To re-establish steady-state, we introduce the rest terms.*
> *We restructured the Sections "Steady-state assumption" and "Closure of the budget" in the manuscript and merged them together. We also added the above explanation to better justify the rest terms.*
>
> ***Changes in manuscript:***
> *Thus, the state-state for the reduced HO_x and H reaction system (Tables 1 and 2) is not completely fulfilled.*
> *But steady-state between production and loss is crucial for the tagging method for short-lived species. To re-establish steady-state, it would be necessary to include the complete HO_x and H chemistry in the tagging method. However, this is not possible as the tagging method does not apply to all reactions of the HO_x and H chemistry (for examples see Appendix A). Consequently, we introduce rest terms resOH, resHO2 and resH for OH, HO_2 and H to compensate for the deviations from steady-state.*

Significant work is required by the authors to refine and clarify the manuscript. I suggest much more proof reading and editing are necessary prior to any resubmission.

> *We thoroughly edited the manuscript based on the reviewer comments. We hope that it now better suits the reviewer's expectations.*

3 Technical Corrections

1. I personally did not like the authors stating the species chemical formula after the name, without using either parentheses or parenthetical commas, e.g.
   The radicals hydroxyl OH and hydroperoxyl HO_2 are crucial for the atmospheric chemistry.
   rather than
   The radicals hydroxyl (OH) and hydroperoxyl (HO_2) are crucial for the atmospheric

chemistry.
or
The radicals hydroxyl, OH, and hydroperoxyl, HO_2, are crucial for the atmospheric chemistry.
This first format is used throughout the document (including the abstract). I would advise the authors to correct this to one of the others.

Thank you. We changed the notation to parentheses.

2. Page 1, line 16: remove "the" before "atmospheric chemistry".

   Done.

3. Page 3, line 5: remove "the" before HO_x.

   Done.

4. Page 4, line 6: could the authors please explain what a "cataster" is?

   We changed the word to inventory.

5. Page 4, lines 20-21: I would suggest either "The mechanism in V1.0" or "The V1.0 mechanism".

   We changed the wording.

6. Page 5, lines 6-7: I don't quite understand what the authors mean by "Each reaction occurring in a simulation was precisely added up" in the context of the paragraph. Could the authors please re-phrase this?

   We have reformulated the corresponding sentences.

   Changes in manuscript:
   Most reaction rates used in the tagging method corresponds to the production and loss rates directly provided by the chemical scheme MECCA of EMAC.

7. Page 5, line 16: I would not use the phrase "boil down". I would suggest using "reduce" instead.

   We changed the word.

8. There is discussion in Section 3.2 about the relative contributions of various reactions to the OH and HO_2 budgets. It might be helpful to also visualise this, perhaps using bar- or pie-charts, perhaps in the Supplementary Information?

   Thank you for this hint. We added the amounts of the relative contributions of the mentioned reactions to the text.

   Changes in manuscript:
   The reactions which are important in the troposphere are indicated in Table 1. As stated above, reaction (1) of H and O_2 dominates the HO_2 production in the troposphere. It produces 49 % of tropospheric HO_2. In V1.0, only part of this HO_2 source was regarded (see Sect. 3.1). The most important HO_2 loss is the reaction with NO (reaction 14) followed by the reaction with itself producing H_2O_2 (reaction 3) which accounts for 32 % and 12 % of tropospheric HO_2 loss. The production via H2O and $O(^1D)$ produces about

21 % of tropospheric OH (reaction 2). The excited oxygen radical ($O(^1D)$) originates from the photolysis of O_3. Also reaction (14) of NO and HO_2 produces 32 % of tropospheric OH. OH is mostly destroyed by CO (reaction 11, 38 %) followed by NMHC (reaction 21, 25 %).

In the stratosphere different chemical reactions become important. Here, OH is mainly destroyed by O_3, producing 40 % of stratospheric HO_2. The reaction is partly counteracted by the reaction (14) which produces 21 % of OH and destroys 24 % of HO_2. Since large quantities of O3 are found in the stratosphere, O_3 or the excited oxygen radical ($O(^3P)$) destroys about 62 % of HO_2. Reactions with NMHC, CO and CH_4 play only a minor role in the stratosphere.

9. Page 13 equations 17, 18, 23, and Page 14 equation 24: Why does the term resOH=n appear in both equation 17 and 23, and the terms resHO_2=n and resH=n appear in both 18 and 24. Looking at equations 15 and 16, shouldn't these terms appear only once each?

   Yes, this is right. We deleted them in eqs. (23) and (24).

10. I was slightly frustrated by the use of different scales in the various sub-plots in Figure 2 (and also 3). While I appreciate there are orders of magnitude differences between various sectors, it would be helpful to have these all plotted on the same scale (with different common scales between Figures 2 and 3). I think that it would be helpful, as these are contrasted with Figures A1 and A2, which do have a common scale for all the sub-plots of each figure.

    Thank you for pointing this out. We changed these figures and put them on a common scale.

11. In Figures 4 and 5, is the use of the 0.1 to 0.5 (and -0.5 to -0.1) band useful? The authors explicitly discount changes this small, and would changes on these levels even be significant?

    This is a good point. We deleted these figures and replaced them to a direct comparison with V1.0 as it was recommended by reviewer #1.

12. In Figures 4 and 5, could the authors explain the jagged feature seen in the OH biomass burning, the HO_2 N_2O decomposition, and to a certain extent, the HO_2 lightning plots?

    We exchanged these figures to a direct comparison to V1.0 as it was recommended by reviewer #1. The jagged features resulted from divisions with small numbers.

13. Page 19, line 4: I believe the authors mean "no large changes", not "no changes", as this is the wording they use in two other places in the manuscript.

    Yes, we mean "no large changes". So we changed it. Thank you.

14. Page 19, line 11: "long-lived tracers".

    Thank you for this hint. We corrected it.

15. Page 19, line 11: I would not use "Exemplary", and would instead use "For example".

    We changed it.

16. Page 19, last paragraph: Is this referencing the plots in the Supplementary Information? If so, please say so.

    Yes, indeed. We included the corresponding references.

17. In the Supplementary Information, I would suggest labelling the figures as S1, S2 etc., especially since these figures should be referenced in the main text in some way, and it would be confusing otherwise.

    This is a good point. We changed the labels of the supplement.

List of relevant changes

- Restructuring of the manuscript, case “tag” as baseline of manuscript, move discussion of omitted reactions in appendix
- Better explanations on interaction between tagging method of short-lived and long-lived species, addition of sketch about interaction (Fig. 1)
- Removal of former Fig. 1 and corresponding discussion about seasonal cycle
- Better justification of introduction of rest terms, merging Section “Steady-state assumption” and “Closure of the budget”
- Better representation of steady-state assumption, inclusion of discussion about steady-state assumption of H
- Better representation of results, modified figures and text passages, clearer explanations
- Extended conclusion

An advanced method of contributing emissions to short-lived chemical species (OH and HO_2): The TAGGING 1.1 submodel based on the Modular Earth Submodel System (MESSy 2.53)

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Abstract. To mitigate human impact on climate change, it is essential to determine the contribution of emissions to the concentration of ~~certain~~ trace gases. In particular, source attribution of short-lived species such as OH and HO_2 is important as they play a crucial role for atmospheric chemistry. This study presents an advanced version of ~~the~~ a tagging method for OH and HO_2 (HO_x) which attributes HO_x ~~concentration~~ concentrations to emissions. While the former version V1.0 only considered 12 reactions in the troposphere, the new version V1.1, presented here, takes 19 reactions in the troposphere into account. For the first time, also the main chemical reactions for the HO_x chemistry in the stratosphere are regarded (in total 27 reactions). To fully take into account the main HO_2 source by the reaction of H and O_2, the tagging of H radical is introduced. In order to ~~close the budget between the sum of all contributions and the total concentration, we explicitly~~ ensure the steady-state assumption, we introduce rest terms ~~,~~ which balance the deviation of HO_x production and loss. This closes the budget between the sum of all contributions and the total concentration. The contributions to ~~the~~ OH and HO_2 ~~concentration~~ obtained by the ~~improved~~ advanced tagging method V1.1 ~~deviates~~ deviate from V1.0 in certain source categories. For OH, major changes are found in the categories ~~of biomass burningemissions~~biomass burning, biogenic emissions and methane decomposition. For HO_2, the contributions differs strongly in the categories biogenic ~~emission~~ emissions and methane decomposition. ~~The tagged long-lived species of~~ As HO_x reacts with ozone (O_3), carbon monoxide (CO), reactive nitrogen compounds (NO_y), non-methane hydrocarbons ~~NMHC~~ (NMHC) and peroxyacyl nitrates ~~PAN~~ (PAN), the contributions to these species are also modified by the advanced HO_x tagging method V1.1. The contributions to NO_y, NMHC and PAN show only little changes~~.~~, whereas O_3 from biogenic emissions and methane decomposition ~~decreases~~ increases in the tropical troposphere. Variations for CO from ~~lightning, biogenic and methane decomposition are~~ biogenic emissions and biomass burning are only found in the Southern Hemisphere.

1 Introduction

The radicals hydroxyl ~~OH and hydroperoxyl~~ (OH) and hydroperoxyl (HO_2) are crucial for ~~the~~ atmospheric chemistry. Both radicals are very reactive and have a lifetime of only a few seconds. OH is frequently converted to HO_2 and vice versa. Thus,

~~the~~ OH and HO_2 radicals are closely linked and often referred together as ~~the~~ chemical family HO_x. The ratio of OH to HO_2 in an air parcel strongly depends on the chemical background, in particular on the composition of nitrogen oxides NO_x (= NO + NO_2) and non-methane hydrocarbons ~~NMHC~~ (NMHC) (Heard and Pilling, 2003).

HO_x impacts ~~the~~ global warming and ~~the~~ local air quality in various ways: Reacting with greenhouse gases such as methane (CH_4~~and ozone~~) and ozone (O_3), OH reduces their atmospheric residence time (e.g. Stevenson et al. (2006); Voulgarakis et al. (2013); Righi et al. (2015)). Hence, HO_x controls the impact of CH_4 and O_3 on global warming. Moreover, being the main oxidizer in the troposphere, OH is involved in the decomposition of pollutants ~~,~~ as well as in the production of ground-level ozone, photochemical smog and secondary organic aerosols (e.g. Lawrence et al. (2001); Heard and Pilling (2003)). Consequently, to quantify ~~the~~ human impact on ~~the~~ climate and air quality, it is essential to understand the distribution and variability of OH and HO_2 in the atmosphere.

However, the determination of OH and HO_2 concentrations in the atmosphere is still challenging due to their short lifetimes. In field campaigns HO_x concentrations are measured on a local scale which is generally difficult to compare with global models ~~(e. g. Ren et al. (2003); Olson et al. (2006)).~~ (e.g. Ren et al., 2003; Olson et al., 2006) . For certain environments, such as marine boundary layer, model studies compare well with ~~the~~ measurements. Other regions, such as unpolluted forest areas, show large discrepancies (Heard and Pilling, 2003; Stone et al., 2012). On ~~a~~ regional and global scale, no direct HO_x measurement is available. So far, OH can only be estimated indirectly by measurements and emission rates of methyl chloroform (CH_3CCl_3) (Prinn et al., 2005). As emissions of CH_3CCl_3 steadily decline, ~~Liang et al. (in press, 2017)~~ Liang et al. (2017) suggest an alternative method: They combine several trace gases such as CH_2F_2, CH_2FCF_3, CH_3CHF_2 and $CHClF_2$ in a gradient-trend based two-box model approach to derive a global OH concentration of $11.2 \cdot 10^5$ molec cm^{-3}. Overall, global ~~climate-chemistry~~ chemistry climate models estimate a tropospheric OH concentration of around $11 \cdot 10^5$ molec cm^{-3} (Naik et al., 2013), which compares well with the observation-based results from Prinn et al. (2005) and Liang et al. (2017).

To mitigate ~~the~~ human impact on climate change or pollution in general, it is crucial to determine the contribution of ~~a specific~~ an emission sector to the concentration of certain chemical species ~~(Grewe et al., 2012)~~ (Grewe et al., 2012; **?**) . To do so, we use ~~the so called~~ a "tagging" method~~(Grewe et al., 2010, 2017)~~ : the theoretical framework of this tagging method is given in Grewe et al. (2010) and Grewe (2013) , whereas the implementation is described in (Grewe et al., 2017) . This method splits up all chemical species which are important for O_3 production and destruction into ten source categories: emissions from anthropogenic non-traffic (e.g. industry and households), road traffic, ~~ship traffic, air traffic~~shipping, aviation, biogenic sources, biomass burning, lightning, methane (CH_4) and nitrous oxide (N_2O) decompositions and stratospheric ozone production. Subsequently, the contributions of theses sources to the concentrations of O_3, CO, OH, HO_2, peroxyacyl nitrates ~~PAN~~(PAN), reactive nitrogen compounds (NO_y~~(~~, e.g. NO, NO_2, HNO_4, ...) and non-methane hydrocarbons ~~NMHC~~ (NMHC) are diagnosed. The contribution calculations are based on chemical reaction rates, online emissions (e.g. lightning), offline emissions (e.g. road traffic) and ~~depositions~~ deposition rates. It considers the competition of NO_y, CO and NMHC in producing and destroying O_3.

The tagging method of the long-lived species O_3, CO, PAN, NO_y and NMHC ~~are tagged in a different way than~~ and of the short-lived species OH and HO_2 base on the same principles of apportioning the contributions. (In this study, O_3, CO, PAN,

NO_y and NMHC are denoted as long-lived species because their atmospheric lifetime is significantly longer then the lifetime of OH and HO_2.) ~~For these~~ However, the implementation for long-lived and short-lived species differs. For the long-lived species, each source ~~specific~~ tracer is transported, receives the corresponding online or offline emissions, is deposited and reacts with other species. Based on these processes, the tagging method determines the concentration of the source ~~specific tracers.~~ tracers. A detailed description of the implementation of the tagging method for long-lived species is given in Grewe et al. (2017) .

However, the short-lived species HO_x are not transported and experience neither emissions nor deposition. Thus, the ~~tagging method~~ same implementation of the tagging method as for long-lived species is not ~~applicable~~possible. Tsati (2014) and Grewe et al. (2017) introduced a modified ~~tagging method for~~ approach for tagging HO_x: since the lifetime of OH and HO_2 is very short, a steady-state between the production and destruction of OH and HO_2 is assumed. Using the main chemical reactions of ~~the~~ HO_x chemistry, the ~~contribution~~ contributions of each source category to OH and HO_2 ~~can be~~ are determined.

~~But the HO_x tagging method V1.0,~~ The contributions to long-lived and short-lived species are closely linked (see Fig. 1). For example, the reaction

$$OH + O_3 \longrightarrow HO_2 + O_2$$

involves the long-lived species O_3 and the short-lived species OH and HO_2. Hence, this reaction is considered in the implementation of the tagging method for long-lived and short-lived species. The contribution of, for example, shipping emissions to O_3 influences the contribution of shipping emissions to HO_2: the higher the contribution to O_3 is the more HO_2 is attributed to shipping emissions. Furthermore, OH from shipping emissions destroys O_3 and thus reduces the contribution of shipping emissions to O_3.

The implementation of the tagging method for the short-lived species HO_x, presented by Grewe et al. (2017), is referred to HO_x tagging method V1.0. It did not consider all relevant reactions for the production and loss of HO_x. Especially, the reactions which are important in the stratosphere were not taken into account. Moreover, the ~~budget of the sum of all tagged~~ steady-state assumption between HO_x ~~species and the total HO_x concentrations was not closed~~production and loss was not fulfilled. In this study, we present a revised version V1.1 of the HO_x tagging method, largely improving these shortcomings. It includes the main chemical reactions of ~~the~~ HO_x chemistry in the troposphere and stratosphere. This is enabled by introducing the tagging of the hydrogen radical ~~H~~(H). Special care is taken for the ~~closure of the budget~~steady-state assumption.

The paper is structured as follows: After introducing the model setup in Section 2, we present the advanced HO_x tagging ~~mechanism~~ method V1.1 in Section 3. In Section 4, the results are compared with the tagging ~~mechanism~~ method V1.0 by Grewe et al. (2017). Finally, Section 5 concludes the method and the results of this study.

2 Model description of EMAC and MECO(n)

To evaluate the further developed HO_x tagging ~~mechanism~~ method we use the same model setup as Grewe et al. (2017). A global climate simulation is performed with the ECHAM/MESSy Atmospheric Chemistry (EMAC) ~~climate-chemistry~~ chemistry climate model. EMAC is a numerical chemistry and climate simulation system that includes submodels describing tropospheric and middle atmosphere processes and their interaction with oceans, land and human influences (Jöckel et al.,

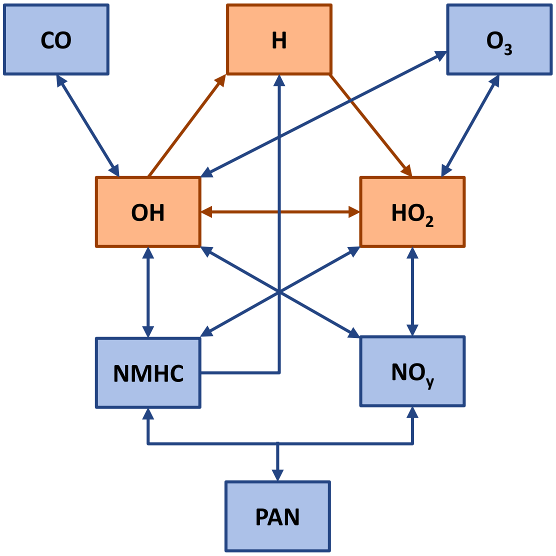

Figure 1. Sketch of chemistry used in advanced tagging mechanism V1.1. Blue boxes indicate tagged long-lived species, orange boxes display tagged short-lived species.

2010). It uses the second version of the Modular Earth Submodel System (MESSy2.53) to link multi-institutional computer codes. The core atmospheric model is the 5th generation European Centre Hamburg general circulation model (ECHAM5, Roeckner et al. (2006)). For the present study we apply EMAC in the T42L90MA-resolution, i.e. with a spherical truncation of T42 (corresponding to a quadratic Gaussian grid of approx. 2.8° by 2.8° in latitude and longitude) with 90 vertical hybrid pressure levels up to 0.01 hPa. For the simulation presented in this study, the time span of July ~~2009 to December 2010~~ 2007 to December 2008 is considered: half a year as a spin-up and one year for the analysis.

For the chemical scheme, we use the submodel MECCA (Module Efficiently Calculating the Chemistry of the Atmosphere) which is based on Sander et al. (2011) and Jöckel et al. (2010). The chemical mechanism includes 218 gas phase, 12 heterogeneous and 68 photolysis reactions. In total 188 species are considered. It regards the basic chemistry of OH, HO_2, O_3, CH_4, nitrogen oxides, alkanes, alkenes, chlorine and bromine. Alkynes, aromatics and mercury are not considered.

Total global emissions of lightning NO_x are scaled to approximately 4 Tg(N) a^{-1} (parametrized ~~after~~ according to Grewe et al. (2001)). The submodel ONEMIS (Kerkweg et al., 2006) calculates NO_x emissions from soil (parametrized ~~after~~ according to Yienger and Levy (1995)) and biogenic C_5H_8 emissions (parametrized ~~after~~ according to Guenther et al. (1995)). Direct CH_4 emissions are not considered, instead pseudo-emissions are calculated using the submodel TNUDGE (Kerkweg et al., 2006). This submodel relaxes the mixing ratios in the lowest model layer towards observations by Newtonian relaxation (more details are given by Jöckel et al. (2016)).

To show the effect of the HO_x tagging method on a regional scale, a further simulation with the coupled model system MESSyfied ECHAM and COSMO models nested n-times (MECO(n)) is performed. The nested system couples the global

~~chemistry-climate~~ chemistry climate model EMAC online with the regional chemistry climate model COSMO/MESSy (Kerkweg and Jöckel, 2012a, b). To test the HO_x tagging in MECO(n), we conduct a simulation using one COSMO/MESSy nest over Europe with a resolution of 0.44°. EMAC is applied in a horizontal resolution of T42 with 31 vertical levels. The period from July 2007 to December 2008 is simulated. The setup of the simulation is identical to the one described in Grewe et al. (2017). A detailed chemical evaluation of the setup is given in Mertens et al. (2016).

Both model simulations are based on the quasi chemistry-transport model (QCTM) mode in which the chemistry is decoupled from the dynamics (Deckert et al., 2011). The anthropogenic emissions are taken from the MACCity emission ~~cataster~~ inventory (Granier et al., 2011). The TAGGING submodel (as described by Grewe et al. (2017)) is coupled to the detailed chemical solver MECCA from which it obtains information about tracer concentrations and reaction rates. Based on this information, it calculates the contributions of source categories to O_3, CO, NO_y, PAN and NMHC concentration. The contributions of OH and HO_2 are calculated with the advanced method V1.1 presented in the next section. The implementation is based on MESSy2.53 and will be available in MESSy2.54.

3 Tagging method of short-lived species

3.1 Tagging method V1.0

The tagging ~~mechanism~~ method V1.0 described by Grewe et al. (2017) determines the contribution of source categories to O_3, NO_y, CO, NMHC, PAN, OH and HO_2 concentrations. Ten source categories are considered and every species included in the tagging method is decomposed into these categories: For example, the concentration of O_3 is split up into O_3 from anthropogenic non-traffic (e.g. industry) emissions (O_3^{ant}), road traffic emissions (O_3^{tra}), ship emissions (O_3^{shp}), air traffic emissions (O_3^{air}), biogenic emissions (O_3^{bio}), biomass burning (O_3^{bb}~~, lightning~~), lightning (O_3^{lig}), methane decomposition ($O_3^{CH_4}$), nitrous oxide decomposition ($O_3^{N_2O}$) and stratospheric ozone production (O_3^{str}). These tagged species go through the same chemical reactions and the same deposition loss processes as O_3. The tagging method uses a combinatoric approach to determine the contributions: It redistributes the production and loss rates of each species to the ten source categories according to the concentrations of the tagged species. Details on the tagging theory and implementation in EMAC and MECO(n) are found in Grewe (2013) and Grewe et al. (2017), respectively.

For the first time, V1.0 determined the contribution of source categories to OH and HO_2 concentrations. The ~~mechanism~~ tagging method V1.0 was based on 12 reactions for the HO_x chemistry (reactions marked with "o" in last column of Table 1). It included the main production and loss reactions of HO_x with O_3, NO_y, NMHC, CO and CH_4. V1.0 only regarded reactions which are important in the troposphere. Reactions which mainly occur in the stratosphere were not taken into account. However, the main HO_2 production by the reaction (1) $H + O_2 \longrightarrow HO_2$ ~~was not explicitly~~ (see Table 1) was not regarded. It was combined with reaction (11) $CO + OH \longrightarrow H + CO_2$ (see Table 1) to

$$\begin{aligned} &CO + OH \longrightarrow CO_2 + H \xrightarrow{O_2} CO_2 + HO_2 \\ &\qquad \Longrightarrow CO + OH \xrightarrow{O_2} CO_2 + HO_2 \end{aligned}$$

$$CO + OH \longrightarrow CO_2 + H$$

$$\xrightarrow{O_2} CO_2 + HO_2$$

$$\Longrightarrow CO + OH \xrightarrow{O_2} CO_2 + HO_2$$

But not all H radicals in the troposphere are produced by the reaction of CO + OH. Also the reactions (7) OH + O(^{3}P), (10) H_2 + OH and (~~31) photolyses of formaldehyde HCHO~~ 28) HCHO + *hv* produce H (Table 2). These reactions were neglected in V1.0. Thus, only 80 % of the H production and therefore only 80 % of the HO_2 production by reaction (1) was considered in the troposphere. In the stratosphere, the reaction of CO + OH becomes less important and most of H is produced by reactions (7) and (~~11~~28). Consequently, only 6 % of the H and also of HO_2 production by reaction (1) was regarded by this approach. (Numbers are derived from a EMAC simulation as described in Sect. 2.)

In the troposphere, the most important reactions not covered in V1.0 are reaction (1) H + O_2 as well as reaction (15) NO_2 + HO_2 and (18) decomposition of HNO_4. In the stratosphere, reactions (1) H + O_2, (5) HO_2 + O(^{3}P) and (7) OH + O(^{3}P) play a leading role and were not included in V1.0.

Most reaction rates ~~were obtained directly by the MECCA mechanism~~ used in the tagging method corresponds to the production and loss rates directly provided by the chemical scheme MECCA of EMAC. ~~Each reaction occurring in a simulation was precisely added up.~~ However for reactions with NMHC, the reaction rates were obtained indirectly. The reaction rate of OH with NMHC (reaction ~~22~~21, Table 1) was determined via the production rates of CO by assuming that each reaction of OH with NMHC produces one CO molecule. This method neglects all intermediate oxidation reactions of NMHC and considers only these reactions when NMHC is finally oxidized to CO. For the reaction rates of NO_y and HO_2 with NMHC (reaction 22 and 23), only the reaction of HO_2 with methylperoxy radical (CH_3O_2) was considered.

~~For the~~ To derive the contributions to OH and HO_2, steady-state between HO_x production and loss ~~, a steady state was assumed: the production equaled the loss. Based on this assumption, the source contributions to the concentrations of OH and HO_2 were determined.However~~was assumed. However, the steady-state assumption was not completely fulfilled for V1.0 (see Sect. 3.4). Moreover, the sum over the contributions of ~~all~~ the ten source categories to the OH and HO_2 concentrations did not equal the total OH and HO_2 concentrations. It deviated by about 70 %. ~~To close the budget and to extend to method to the stratosphere, an advanced HO_x tagging method V1.1 is developed in this study.~~

3.2 Reduced HO_x reaction system V1.1

OH and HO_2 react with many chemical species. To reduce the calculation time of a simulation, we ~~boil down~~ reduce the HO_x chemistry used in chemical scheme MECCA to the most important reactions which occur in the troposphere and stratosphere. We consider only reactions with a tropospheric or stratospheric annual mean reaction rate larger than $10^{-15}\,\mathrm{mol\,mol^{-1}s^{-1}}$ (~~Reactions 1 to 30 in~~ see Table 1). Hence, we increase the number of reactions from 12 (V1.0) to ~~30~~ 27 (V1.1), which still constitutes a reduced set of reactions compared to the ~~chemical scheme~~ full chemical scheme MECCA used in EMAC. In the following, we call this set *reduced HO_x reaction system V1.1*.

	reaction		
1	$H + O_2$	$\longrightarrow$	HO_2
2	$H_2O + O(^1D)$	$\longrightarrow$	$2\,OH$
3	$HO_2 + HO_2$	$\longrightarrow$	$H_2O_2 + O_2$
4	$HO_2 + O_3$	$\longrightarrow$	$OH + 2\,O_2$
5	$HO_2 + O(^3P)$	$\longrightarrow$	$OH + O_2$
6	$OH + O_3$	$\longrightarrow$	$HO_2 + O_2$
7	$OH + O(^3P)$	$\longrightarrow$	$H + O_2$
8	$HO_2 + OH$	$\longrightarrow$	$H_2O + O_2$
9	$H_2O_2 + OH$	$\longrightarrow$	$H_2O + HO_2$
10	$H_2 + OH$	$\longrightarrow$	$H_2O + H$
11	$CO + OH$	$\longrightarrow$	$H + CO_2$
12	$CH_4 + OH$	$\longrightarrow$	$CH_3 + H_2O$
13	$ClO + OH$	$\longrightarrow$	$0.94\,Cl + 0.94\,HO_2 + 0.06\,HCl + 0.06\,O_2$
14	$NO + HO_2$	$\longrightarrow$	$NO_2 + OH$
15	$NO_2 + HO_2$	$\longrightarrow$	HNO_4
16	$NO + OH$	$\longrightarrow$	$HONO$
17	$NO_2 + OH$	$\longrightarrow$	HNO_3
18	HNO_4	$\longrightarrow$	$NO_2 + HO_2$
19	~~$H_2O_2 + h\nu \longrightarrow 2\,OH$ R_{19} x - 20~~ $HONO + h\nu$	$\longrightarrow$	$NO + OH$
~~21~~ 20	$HNO_3 + h\nu$	$\longrightarrow$	$NO_2 + OH$
~~22~~ 21	NMHC + OH	$\longrightarrow$	NMHC
~~23~~ 22	NMHC + HO_2	$\longrightarrow$	NMHC
~~24~~ 23	NMHC + NO_y	$\longrightarrow$	HO_2 + NMHC + NO_y
~~25~~ 24	NMHC + OH	$\longrightarrow$	NMHC + HO_2
~~26~~ 25	NMHC + $h\nu$	$\longrightarrow$	NMHC + HO_2
~~27~~ 26	$ClO + HO_2$	$\longrightarrow$	$HOCl + O_2$
~~28~~ 27	~~$HOCl + h\nu \longrightarrow OH + Cl$ R_{28} x - 29~~ $BrO + HO_2$	$\longrightarrow$	$HOBr + O_2$

~~30 $HOBr + h\nu \longrightarrow OH + Br$ R_{30} x -~~ height

Table 1. Reduced HO$_x$ reaction system V1.1 ~~. Main reactions which describe~~ describes the main reactions of HO$_x$ chemistry in troposphere and stratosphere. These 27 reactions are used for the tagging method V1.1. In the column "tropos." ("~~stratosp~~stratos.")~~the reaction .~~, reactions which are important in the troposphere (stratosphere) are marked. In the column "V1.1", reactions marked with "o" were already included in V1.0. Reactions marked with "x" are added in V1.1. Reactions marked with "(x)" were only partly taken into account in V1.0. ~~Reactions marked with "-"~~ The numbers of reactions are ~~excluded as it is not possible to apply~~ referenced in the ~~tagging theory~~text.

The reactions which are important in the troposphere are ~~explicitly~~ indicated in Table 1. As stated above, ~~the~~ reaction (1) of H and O_2 dominates the HO_2 production in the troposphere. ~~In the mechanism~~ It produces 49 % of tropospheric HO_2. In V1.0, only part of this HO_2 source was regarded (see Sect. 3.1). The most important HO_2 loss is the reaction with NO (reaction 14) followed by the reaction with itself producing H_2O_2 (reaction 3) which accounts for 32 % and 12 % of tropospheric HO_2 loss. The production via H_2O and $O(^1D)$ produces ~~most of the OH which can be found in the troposphere~~ about 21 % of tropospheric OH (reaction 2). The excited oxygen radical ($O(^1D)$) originates from the photolysis of O_3. Also reaction (14) of NO and HO_2 produces ~~a major part~~ 32 % of tropospheric OH. OH is mostly destroyed by CO (reaction 11, 38 %) followed by ~~the destruction by~~ NMHC (reaction ~~22~~21, 25 %).

In the stratosphere different chemical reactions become important. Here, OH is mainly destroyed by O_3, producing ~~most of the~~ 40 % of stratospheric HO_2~~in the stratosphere~~. The reaction is partly counteracted by the reaction (14) which produces 21 % of OH and destroys 24 % of HO_2. Since large quantities of O_3 ~~can be~~ are found in the stratosphere, O_3 or the excited oxygen radical ($O(^3P)$~~destroys~~) destroys about 62 % of HO_2. Reactions with NMHC, CO and CH_4 play only a minor role in the stratosphere.

~~The reactions~~ Reactions of OH and HO_2 with chlorine and bromide were not considered in V1.0. We add these reactions, which ~~occur~~ take place only in the stratosphere, to the tagging ~~mechanism~~ method V1.1. ~~The photolysis of H~~Reactions (21) to (25) involve the chemical family NMHC which contains several species such as formaldehyde (HCHO), ethylene (C_2H_4) and propane (C_3H_8). The rate for reaction (21) is determined by adding up the rates of all reactions of OH with each single species of the family NMHC. Reaction rate (23) contains all rates of the reactions between the species of the chemical families NO_y and NMHC. All reaction rates are directly derived by MECCA mechanism of EMAC.

Table 1 does not consider all reactions with annual reaction rates larger than 10^{-15} $\mathrm{mol\,mol^{-1}s^{-1}}$. The photolysis of hydrogen peroxide (H_2O~~$_2$ (reaction 19) , HOCl (reaction 28) and HOBr (reaction 30) are not considered in the~~ $_2$), hypochlorous acid (HOCl) and hypobromous acid (HOBr) are excluded from the reduced HO_x ~~tagging mechanism~~ reaction system V1.1 ~~because they do not fulfil the steady-state assumption (see Sect. 3.3 for more details).~~ as the tagging method can not be applied. The specific reasons are explained in Appendix A.

3.3 ~~Steady-state assumption~~

~~To correctly describe the HO_x chemistry, it is crucial that HO_x production and loss of the reduced HO_x reaction system V1.1 in Table 1 (almost) equal the HO_x production and loss of the complete HO_x chemistry. Fig. **??** compares the seasonal cycle (year 2010)of the HO_x production and loss of the reduced reaction system for the tagging mechanisms V1.0 and V1.1 and the total production and loss rates derived from the MECCA mechanism in EMAC. The production and loss rates are obtained from an EMAC simulation following the setup described in Sect. 2. Furthermore, Fig. **??** shows the OH production rate as a sum of all 30 reactions (indicated with "all") and as a sum of the 27 reactions (without reaction 19, 28 and 30) which are finally used in the tagging mechanism (indicated with "tag") . The annual mean values are further summarized in Table 3. In this section, we only discuss the OH production rate of all 30 reactions ("all"). The implications of the OH production rate "tag" with 27 reactions are discussed in Sect. 3.3.~~

~~Monthly mean of OH and HO_2 production and loss rates for the total HO_x production and loss (derived from the MECCA scheme in EMAC) and for the production and loss of the reduced reaction system of the tagging mechanism V1.0 and V1.1. (a) and (c) shows the rates for troposphere, (b) and (d) for the stratosphere. For OH, also the production rate for all reactions listed in Table 1 (indicated with "all") and these which are finally used in the tagging mechanism (without reaction (19), (28) and (30), indicated with "tag") are shown.~~

~~production loss production loss total - MECCA tropos. $5.11 \cdot 10^{-14}$ $5.11 \cdot 10^{-14}$ $5.13 \cdot 10^{-14}$ $5.12 \cdot 10^{-14}$ *stratos.* *$2.78 \cdot 10^{-13}$* *$2.78 \cdot 10^{-13}$* *$2.48 \cdot 10^{-13}$* *$2.48 \cdot 10^{-13}$* reduced - V1.1 all tropos. $5.01 \cdot 10^{-14}$ $5.07 \cdot 10^{-14}$ $4.95 \cdot 10^{-14}$ $5.11 \cdot 10^{-14}$ *stratos.* *$2.54 \cdot 10^{-13}$* *$2.76 \cdot 10^{-13}$* *$2.47 \cdot 10^{-13}$* *$2.48 \cdot 10^{-13}$* reduced - V1.1 tag tropos. $4.58 \cdot 10^{-14}$ *stratos.* *$2.50 \cdot 10^{-13}$* reduced - V1.0 tropos. $4.54 \cdot 10^{-14}$ $4.95 \cdot 10^{-14}$ $3.10 \cdot 10^{-14}$ $4.38 \cdot 10^{-14}$ *stratos.* *$8.60 \cdot 10^{-14}$* *$1.30 \cdot 10^{-13}$* *$1.19 \cdot 10^{-13}$* *$8.30 \cdot 10^{-14}$* Annual mean of OH and HO_2 production and loss rates in mol mol^{-1} s^{-1} for the total HO_x production and loss (derived from the MECCA scheme in EMAC) and for the production and loss of the reduced reaction system of the tagging mechanism V1.0 and V1.1. For OH, also the production rate for all reactions listed in Table 1 (indicated with "all") and these which are finally used in the tagging mechanism (without reaction (19), (28) and (30), indicated with "tag") are shown. The first row gives the rates for the troposphere, the second row for the stratosphere (written in italic).~~

~~In general, the total OH production (derived by MECCA) equals the total OH loss in the troposphere and stratosphere. The same holds for HO_2. For this reason, the grey line for the total loss rate in Fig. **??** is not visible since it overlaps with the total production rate (black line) .~~

~~In the troposphere, the yearly mean of the total OH production and loss rates are $5.11 \cdot 10^{-14}$ mol mol^{-1} s^{-1} (Fig. **??**a, Table 3). The OH loss of the reduced HO_x reaction system V1.1 represents almost the total OH loss occurring in the troposphere. The yearly averaged OH loss of V1.1 deviates only by less than 1 from the total OH loss. In contrast, the OH loss of V1.0 deviated by more than 3 from the total OH loss. The OH production for V1.1 ("all") differs by 2 from the total OH production. This is clearly less than for V1.0 which differed by 11 from the total OH production.~~

~~Considering HO_2 in the troposphere, the total loss rate of $5.12 \cdot 10^{-14}$ mol mol^{-1} s^{-1} is very well reflected by the reduced HO_x reaction system V1.1. It deviates only 0.1 from the total HO_2 loss (thus the orange line is not visible in Fig. **??**c). In contrast, the HO_2 loss of V1.0 differed by 15 . The HO_2 production of V1.1 disagrees by 3 , V1.0 by 40 from the total production.~~

~~In the stratosphere, the total OH production of $2.78 \cdot 10^{-13}$ mol mol^{-1} s^{-1} equals the total OH loss. Analogously , HO_2 production of $2.48 \cdot 10^{-13}$ mol mol^{-1} s^{-1} balances the total loss. Since V1.0 was only developed for the troposphere, not all reactions which are important in the stratosphere were considered. Thus, the OH and HO_2 production and loss rates of V1.0 considerably underestimated the total production and loss rates. The OH production of V1.1 misses 9 of the total OH production in the stratosphere. However, the OH loss is presented very well with an error of only 0.7 . The HO_2 loss in the stratosphere is perfectly presented by V1.1. The HO_2 production of V1.1 deviates by only 0.2 from the total HO_2 production.~~

~~All reaction rates, except OH loss and HO_2 production of V1.0, follow a similar seasonal cycle. In V1.0 the rate of reaction (18) and (22) was determined indirectly by the increase and decrease of CO (see Sect. 3.1). It was assumed that for each NMHC which is destroyed by OH a CO molecule is produced. In V1.1 the reaction rate is determined directly by precisely counting~~

~~each single reaction. Thus, OH loss and HO_2 production of V1.1 follow exactly the trend of the total production and loss rates over the year. The deviations between the total production and loss rates and those of V1.1 stay constant over time.~~

~~The reduced HO_x reaction system V1.1 represents very well the total HO_x production and loss in the troposphere and stratosphere. The deviations between the HO_x production and loss of the reduced reaction system and the complete HO_x chemistry are small. Thus, the steady-state assumption for OH and HO_2 of the reduced HO_x reaction system V1.1 is justified.~~

3.3 Deductions of tagged species

To derive how much OH and HO_2 is produced and destroyed by a source category i, the tagging approach described in Grewe et al. (2010, 2017) is used. In general, bimolecular reactions with two chemical species $A + B \longrightarrow C$ are tagged as follows: Each tagged species is split up into its contribution from n source categories $A = \sum_{i=1}^{n} A^i$, $B = \sum_{i=1}^{n} B^i$ and $C = \sum_{i=1}^{n} C^i$. These ~~subspecies~~ contributions (A^i, B^i, C^i) go through the same reactions as their main species (A, B, C). If A from category i reacts with B from category j, then the resulting species C belongs half to the category i and half to the category j:

$$A^i + B^j \longrightarrow \frac{1}{2}C^i + \frac{1}{2}C^j \tag{1}$$

Consequently, the production P and loss L of a species from the category i (here $LossA^i$, $LossB^i$ and $ProdC^i$) ~~can be~~ are determined by regarding all possible combinations of the reaction between A^i and B^j:

$$LossA^i = LossB^i = ProdC^i = k\left(A^iB^i + \sum_{j=1, j\neq i}^{n} \frac{1}{2}A^iB^j + \sum_{j=1, j\neq i}^{n} \frac{1}{2}A^jB^i\right) = \frac{1}{2}R\left(\frac{A^i}{A} + \frac{B^i}{B}\right) \tag{2}$$

with k being the reaction rate coefficient and $R = kAB$ being the respective reaction rate. For unimolecular reactions $A \longrightarrow B + C$, the distribution of categories from the educts is completely passed to the products:

$$LossA^i = \cancel{LossB}ProdB^i = ProdC^i = R\frac{A^i}{A} \tag{3}$$

with the reaction rate $R = kA$.

As described above, the long-lived species O_3, CO, NO_y and NMHC are tagged ~~explicitly. However~~according to tagging method described in Grewe et al. (2017) . Due to limited computational resources, other species such as H~~, H~~$_2$, H_2O_2, CH_4, ClO ~~, BrO , HOCl, HOBr~~ and BrO are not tagged (as in V1.0). Here, ~~we need to apply different methods~~ different approaches are derived to retain the ratio of contribution to total concentration $\frac{A^i}{A}$:

1. If a tagged species reacts with a non-tagged species, the non-tagged species does not contribute and the tagging method for a unimolecular reaction is applied (see equation 3). Examples are reactions (9), (10) and (14).

2. Using the family concept as described in Grewe et al. (2017) allows the assumption that all tags are distributed equally among the species ~~in~~ within the same chemical family. It follows:

$$\frac{NO^i}{NO} = \frac{NO_2^i}{NO_2} = \frac{HNO_4^i}{HNO_4} = \frac{NO_y^i}{NO_y} \tag{4}$$

	reaction			rates	tropos.	stratos.
1	H + O_2	$\longrightarrow$	HO_2	R_1	x	x
7	OH + O(^{3}P)	$\longrightarrow$	H + O_2	R_7		x
10	H_2 + OH	$\longrightarrow$	H_2O + H	R_{10}	x	
11	CO + OH	$\longrightarrow$	H + CO_2	R_{11}	x	x
~~31~~ 28	HCHO + O_2 + hv	$\longrightarrow$	H + CO + HO_2	~~R_{31}~~ R_{28}	x	

Table 2. Reduced H reaction system ~~showing~~ describes the main reactions of H. In the column "tropos." ("~~stratosp~~stratos.")~~the reaction~~ , reactions which are important in the troposphere (stratosphere) are marked. The numbers of the reactions correspond to the numbers in Table 1.

As mentioned in Grewe et al. (2017), all species which are frequently converted back and forth to ozone are considered as an "ozone storage" (?) . These species together with O_3 are lumped into one chemical family "ozone". Both O(^{1}D) and O(^{3}P) belong to this chemical family. Hence, as in Grewe et al. (2017), we apply the family concept and set:

$$\frac{O(^1D)^i}{O(^1D)} = \frac{O(^3P)^i}{O(^3P)} = \frac{O_3^i}{O_3} \tag{5}$$

3. ~~The ratio of the contribution to the total concentration can be determined by introducing an explicit tagging mechanism.~~ In reaction (1), neither H nor O_2 are tagged. To obtain the ~~proper contribution~~ratio $\frac{HO_2^i}{HO_2}$, we set up ~~a specific~~ an extra tagging of H itself. ~~The~~ As the H radical is very reactive, ~~so~~ we assume that H production balances H loss ~~.~~ (see Sect. 3.4). Table 2 presents the main reactions for H which still constitute a subset of full H chemistry implemented in MECCA. Based on Table 2, we ~~can~~ set up the H production $ProdH^i$ and H loss $LossH^i$ for the contribution of a ~~specific~~ source category i:

$$ProdH^i = \cancel{R_1 \frac{H^i}{H}} \cancel{LossH^i =} \frac{1}{2} R_7 \left(\frac{OH^i}{OH} + \frac{O_3^i}{O_3} \right) + R_{10} \frac{OH^i}{OH} + \frac{1}{2} R_{11} \left(\frac{CO^i}{CO} + \frac{OH^i}{OH} \right) + R_{\cancel{31}28} \frac{NMHC^i}{NMHC} \tag{6}$$

$$LossH^i = R_1 \frac{H^i}{H} \tag{7}$$

As mentioned above, the family concept also sets $\frac{HCHO^i}{HCHO} = \frac{NMHC^i}{NMHC}$. Since the steady-state assumption applies for H (see Sect. 3.4), the H production per source category i $ProdH^i$ equals the loss $LossH^i$. After setting eq. ~~7 and 6~~(6) and (7) equal to each other, we obtain:

$$\frac{H^i}{H} = \frac{1}{2} \frac{R_7}{R_1} \left(\frac{OH^i}{OH} + \frac{O_3^i}{O_3} \right) + \frac{R_{10}}{R_1} \frac{OH^i}{OH} + \frac{1}{2} \frac{R_{11}}{R_1} \left(\frac{CO^i}{CO} + \frac{OH^i}{OH} \right) + \cancel{\frac{R_{31}}{R_1}} \frac{R_{28}}{R_1} \frac{NMHC^i}{NMHC} \tag{8}$$

~~To include the OH production by the photolysis of hydrogen peroxide H~~

These different approaches are applied to the reduced HO_x reaction system V1.1 (Table 1) to derive the contributions of source categories to OH and HO_2 ~~O~~in Sect. 3.5.

		OH		HO_2		H	
		prod.	loss	prod.	loss	prod.	loss
total - MECCA	tropos.	0.49	0.49	0.49	0.49	0.24	0.24
	stratos.	*2.78*	*2.78*	*2.48*	*2.48*	*7.09*	*7.09*
reduced - V1.1	tropos.	0.43	0.48	0.47	0.49	0.24	0.24
	stratos.	*2.49*	*2.76*	*2.47*	*2.48*	*7.06*	*5.99*
reduced - V1.0	tropos.	0.43	0.47	0.29	0.42	-	-
	stratos.	*0.86*	*1.30*	*1.19*	*0.84*	-	-

Table 3. Annual mean of OH, HO_2 and H production and loss rates (air mass weighted) in 10^{-13} mol mol^{-1} s^{-1} for the total rates (derived from the complete chemical scheme MECCA in EMAC) and for the rates of the reduced reaction system of the tagging method V1.0 and V1.1. The first row gives the rates for the troposphere, the second row for the stratosphere (written in italic).

3.4 Steady-state assumption

The steady-state assumption of the HO_x chemistry is the basic principle of the tagging method for short-lived species (Tsati, 2014; Grewe et

In steady-state, the production and loss of OH and HO_2 ~~(reaction 19) , we would need to tag H_2O_2.Since the production~~ balance each other. Table 3 shows annual means of HO_x and H production and loss rates of the reduced reaction system for the tagging methods V1.0 and ~~the loss of~~ V1.1 as well as the total production and loss rates derived from the complete chemical scheme MECCA in EMAC. The production and loss rates are obtained from an EMAC simulation following the setup described in Sect. 2. Note that for V1.0 no values for the H ~~$_2O_2$ are not balanced, we can not assume a steady-state. Thus, a similar tagging approach is not valid for H $_2O_2$. Consequently, we exclude the reaction (19) from the HO_x tagging mechanism. This reaction contributes 8 to the total OH production in the troposphere.~~

~~Hypochlorous acid HOCl and hypobromous acid HOBr are photolysed in the stratosphere and produce OH (reaction 28 and 30).However, HOCl and HOBr are not tagged explicitly. Although the steady-state assumption is globally valid, locally the~~ production and loss ~~of HOCl and HOBr are not balanced everywhere. In the stratosphere, for about 65 of the model gridboxes the production deviates by more than 10 from the loss of HOCl and HOBr. In particular, in the transition area between day and night in the polar region, the production deviates strongly from the loss. Also at night where the reactions mostly occur, the steady-state is not fulfilled everywhere. Moreover, since both species are not radicals, their lifetimes can not be assumed to be short. Hence, we can not apply the tagging mechanism, so we have to omit the reactions (28) and (30) for the OH production (see Table 1).~~ are available since the tagging of H was not considered in V1.0.

~~Dropping reaction (19), (28) and (30) leads to a lower OH production . The resulting OH production rate is also given in Fig. ?? and Table 3 ("tag"). Only 90~~

In general, total OH production (derived by MECCA) equals total OH loss in the troposphere and stratosphere. The same holds for HO_2 and H. In the troposphere, the OH loss of V1.1 and V1.0 represents well the total OH loss in the troposphere.

However, the OH production for V1.1 and V1.0 differs by 12 % ~~of~~ from the total OH production~~is represented~~. Considering HO_2 in the troposphere~~; 8 percent points less than all 30 reactions listed in Table 1 (~~, the total production and loss rates are well reflected by V1.1~~"all"). In the stratosphere, the difference is negligible: only 0.5 percent points of the total OH production are not regarded. To compensate this deviation from production and loss rate, we introduce a rest term in Sect. ??~~. In contrast, the HO_2 production and loss of V1.0 differs by 14 % and 41 % from the total rates.

3.5 ~~Closure of the budget~~

~~In~~ In the stratosphere, V1~~.0, the budget of the tagged OH and HO_2 was not closed: the sum over the contributions from all source categories did not balance the total concentration. The averaged deviations for OH and HO_2 in troposphere were about 70~~.1 represents the total rates very well. However, the OH production of V1.1 misses 10 % of the total ~~concentrations. Since the stratosphere was not considered in~~ OH production. Since V1.0 ~~, the deviations were even larger (104 for OH and 89 for~~ was only developed for the troposphere, not all reactions which are important in the stratosphere were considered. Thus, the OH and HO_2 ~~). The improved mechanism~~ production and loss rates of V1.0 considerably underestimated the total production and loss rates.

The reduced H reaction system in V1.1 ~~results in a better closure, but the sum over all source categories still deviates~~ (Table 2) represents the total H production and loss in the troposphere ~~by about 27~~very well. However in the stratosphere, H loss in V1.1 deviates by 17 % ~~(23)~~ from the total ~~OH (HO_2) concentration. In the stratosphere, the deviation is about 21 . This is already a large improvement compared to~~ H loss.

Summing up, the reduced HO_x reaction system V1.1 represents well the total HO_x production and loss in the troposphere and stratosphere. V1.1 reproduces the HO_x chemistry better than V1.0~~, but still not satisfying. Although the tagging mechanism~~. However, OH production in troposphere and stratosphere as well as H loss in the stratosphere of V1.1 ~~includes many new reactions, omitting reaction (19), (28) and (30) still hampers the closure of the budget.~~

~~To close the budget, the steady-state assumption must apply. However, since we consider a~~ deviates from the total rates derived by MECCA. Thus, the state-state for the reduced HO_x and H ~~chemistry mechanism (Table 1 and Table 2) , the production of OH,~~ reaction system (Tables 1 and 2) is not completely fulfilled.

But steady-state between production and loss is crucial for the tagging method for short-lived species. To re-establish steady-state, it would be necessary to include the complete HO_x and H chemistry in the tagging method. However, this is not possible as the tagging method does not apply to all reactions of the HO~~$_2$ and H does not exactly equal the loss (see also Fig. ?? and Table 3). Thus~~$_x$ and H chemistry (for examples see Appendix A). Consequently, we introduce rest terms *resOH*, *resHO*$_2$ and *resH* for OH, HO_2 and H to compensate for ~~these~~ the deviations from steady-state. Each rest term is calculated by subtracting the production rate of the reduced reaction system ~~(Table~~ from the loss rate (Tables 1 and 2)~~from the loss rate.Finally,~~. The resulting rest terms are shown in the Supplement (Fig. S1).

Considering the rest terms ~~have to be divided by the number of source categories *n* to account for the contribution per source category.~~

~~Considering the rest terms *resOH*, *resHO*$_2$ and~~ $resOH$, $resHO_2$ and $resH$ leads to the closure of the budget. In V1.0, the sum over the contributions from all source categories did not balance the total concentration. The averaged deviations for OH and HO$_2$ in troposphere were about 70 % of the total concentrations. Since the stratosphere was not considered in V1.0, the deviations were even larger (104 % for OH and 89 % for HO$_2$). In V1.1, the sum of OH and HO$_2$ now perfectly balances the total OH and HO$_2$ concentrations. The deviations are negligible (below 10^{-4} % for OH and below 10^{-3} % for HO$_2$). Consequently, including the rest terms to the tagging ~~mechanism is mandatory to close the budget.~~ method is mandatory for the steady-state assumption and also closes the budget.

3.5 Determination of HO$_x$ contributions

Taking the above considerations into account, we finally derive the OH and HO$_2$ production and loss terms per source category i. In the reduced HO$_x$ reaction system V1.1 (Table 1), OH is produced by the reactions (2) H$_2$O + O(^{1}D), (4) HO$_2$ + O$_3$, (5) HO$_2$ + O(^{3}P), (14) NO + HO$_2$, (19) ~~H$_2$O$_2$~~ HONO + hv ~~,~~ and (20) ~~HONO + hv, (21)~~ HNO$_3$ + hv~~, (28) HOCl + hv and (30) HOBr + hv. However, reactions (19), (28) and (30) are excluded as H$_2$O$_2$, HOCl and HOBr are not in steady-state (see Sect. 3.3) .~~.

Applying the partitioning described in Sect. 3.3, the OH production for a ~~specific~~ source category i $ProdOH^i$ is determined as follows:

$$\begin{aligned} ProdOH^i =& 2\cdot R_2\frac{O_3^i}{O_3} + \frac{1}{2}R_4\left(\frac{HO_2^i}{HO_2}+\frac{O_3^i}{O_3}\right) + \frac{1}{2}R_5\left(\frac{HO_2^i}{HO_2}+\frac{O_3^i}{O_3}\right) + \frac{1}{2}R_{14}\left(\frac{NO_y^i}{NO_y}+\frac{HO_2^i}{HO_2}\right)\\ &+ R_{\cancel{20}19}\frac{NO_y^i}{NO_y} + R_{\cancel{21}20}\frac{NO_y^i}{NO_y} \end{aligned} \tag{9}$$

OH is destroyed by the reactions (6) OH + O$_3$, (7) OH + O(^{3}P), (8) HO$_2$ + OH, (9) H$_2$O$_2$ + OH, (10) H$_2$ + OH, (11) CO + OH, (12) CH$_4$ + OH, (13) ClO + OH, (16) NO + OH, (17) NO$_2$ + OH, (~~22~~21) NMHC + OH and (~~25~~24) NMHC + OH. The OH loss per source category i $LossOH^i$ is:

$$\begin{aligned} LossOH^i =& \frac{1}{2}R_6\left(\frac{OH^i}{OH}+\frac{O_3^i}{O_3}\right) + \frac{1}{2}R_7\left(\frac{OH^i}{OH}+\frac{O_3^i}{O_3}\right) + \frac{1}{2}R_8\left(\frac{HO_2^i}{HO_2}+\frac{OH^i}{OH}\right) + \frac{1}{2}R_9\left(\frac{HO_2^i}{HO_2}+\frac{OH^i}{OH}\right)\\ &+ R_{10}\frac{OH^i}{OH} + \frac{1}{2}R_{11}\left(\frac{CO^i}{CO}+\frac{OH^i}{OH}\right) + R_{12}\frac{OH^i}{OH} + R_{13}\frac{OH^i}{OH} + \frac{1}{2}R_{16}\left(\frac{NO_y^i}{NO_y}+\frac{OH^i}{OH}\right)\\ &+ \frac{1}{2}R_{17}\left(\frac{NO_y^i}{NO_y}+\frac{OH^i}{OH}\right) + \frac{1}{2}R_{\cancel{22}21}\left(\frac{NMHC^i}{NMHC}+\frac{OH^i}{OH}\right) + \frac{1}{2}R_{\cancel{25}24}\left(\frac{NMHC^i}{NMHC}+\frac{OH^i}{OH}\right) \end{aligned} \tag{10}$$

HO$_2$ is produced by reactions (1) H + O$_2$, (6) OH + O$_3$, (9) H$_2$O$_2$ + OH, (13) ClO + OH, (18) HNO$_4$, (~~24~~23) NMHC + NO$_y$, (~~25~~24) NMHC + OH and (~~26~~25) NMHC + hv. However, H ~~is not explicitly tagged~~ in reaction (1) is not tagged. To be able to determine the HO$_2$ production by reaction (1) $R_1\frac{H^i}{H}$, we apply the introduced H tagging (see Sect. 3.3) and replace $\frac{H^i}{H}$ with equation (8). Besides, reaction (13) constitutes a simplified reaction producing $0.94\cdot HO_2$. Consequently, the HO$_2$ production per source category i $ProdHO2^i$ is~~determined:~~ :

$$\begin{aligned}ProdHO_2^i =& \frac{1}{2}R_6\left(\frac{OH^i}{OH}+\frac{O_3^i}{O_3}\right)+\frac{1}{2}R_7\left(\frac{OH^i}{OH}+\frac{O_3^i}{O_3}\right)+\frac{1}{2}R_9\left(\frac{HO_2^i}{HO_2}+\frac{OH^i}{OH}\right)+R_{10}\frac{OH^i}{OH}\\ &+\frac{1}{2}R_{11}\left(\frac{CO^i}{CO}+\frac{OH^i}{OH}\right)+0.94\cdot R_{13}\frac{OH^i}{OH}+R_{18}\frac{NO_y^i}{NO_y}+\frac{1}{2}R_{\underline{24}23}\left(\frac{NMHC^i}{NMHC}+\frac{NO_y^i}{NO_y}\right)\\ &+\frac{1}{2}R_{\underline{25}24}\left(\frac{NMHC^i}{NMHC}+\frac{OH^i}{OH}\right)+R_{\underline{26}25}\frac{NMHC^i}{NMHC}+R_{\underline{31}28}\frac{NMHC^i}{NMHC} \qquad (11)\end{aligned}$$

The HO_2 loss is determined by reactions (3) HO_2 + HO_2, (4) HO_2 + O_3, (5) HO_2 + O(^{3}P), (8) HO_2 + OH, (14) NO + HO_2, (15) NO_2 + HO_2, (~~23~~22) NMHC + HO_2, (~~27~~26) ClO + HO_2 and (~~29~~27) BrO + HO_2. ~~As HO_2 reacts with itself in reaction (3), $\frac{HO_2^i}{HO_2}$ is counted twice.~~ Hence, the HO_2 loss per source category i $LossHO2^i$ is:

$$\begin{aligned}LossHO_2^i =& R_3\frac{HO_2^i}{HO_2}+\frac{1}{2}R_4\left(\frac{HO_2^i}{HO_2}+\frac{O_3^i}{O_3}\right)+\frac{1}{2}R_5\left(\frac{HO_2^i}{HO_2}+\frac{O_3^i}{O_3}\right)+\frac{1}{2}R_8\left(\frac{HO_2^i}{HO_2}+\frac{OH^i}{OH}\right)\\ &+\frac{1}{2}R_{14}\left(\frac{NO_y^i}{NO_y}+\frac{HO_2^i}{HO_2}\right)+\frac{1}{2}R_{15}\left(\frac{NO_y^i}{NO_y}+\frac{HO_2^i}{HO_2}\right)+\frac{1}{2}R_{\underline{23}22}\left(\frac{NMHC^i}{NMHC}+\frac{HO_2^i}{HO_2}\right)\\ &+R_{\underline{27}26}\frac{HO_2^i}{HO_2}+R_{\underline{29}27}\frac{HO_2^i}{HO_2} \qquad (12)\end{aligned}$$

Sect. ~~??~~ 3.4 shows that the steady-state assumption for OH and HO_2 is justified when the rest terms $resOH$, $resHO_2$ and $resH$ are regarded. Therefore, the rest terms are divided by the number of source categories n to add them to the contributions of a ~~specific~~ category i. In ~~a~~ steady-state, production of OH^i and HO_2^i equals the loss:

$$ProdOH^i - LossOH^i + resOH/n = 0 \qquad (13)$$

$$ProdHO_2^i - LossHO_2^i + resHO_2/n + resH/n = 0 \qquad (14)$$

The equations (13) and (14) ~~can be~~ are rewritten as follows:

$$0 = A^i - L^{OH}\frac{OH^i}{OH}+P^{OH}\frac{HO_2^i}{HO_2}+\frac{resOH}{n} \qquad (15)$$

$$0 = B^i + P^{HO_2}\frac{OH^i}{OH}-\underline{P}L^{HO_2}\frac{HO_2^i}{HO_2}+\frac{resHO_2}{n}+\frac{resH}{n} \qquad (16)$$

with the variables P^{OH}, L^{OH}, P^{HO_2}, L^{HO_2}, A^i and B^i (compare to Grewe et al. (2017) equations (25) to (28)):

$$P^{OH} = \frac{1}{2}R_4+\frac{1}{2}R_5+\frac{1}{2}R_{14}-\frac{1}{2}R_8 \qquad (17)$$

$$L^{OH} = \frac{1}{2}R_6+\frac{1}{2}R_7+\frac{1}{2}R_8+R_9+R_{10}+\frac{1}{2}R_{11}+R_{12}+R_{13}+\frac{1}{2}R_{16}+\frac{1}{2}R_{17}+\frac{1}{2}R_{\underline{22}21}+\frac{1}{2}R_{\underline{25}24} \qquad (18)$$

$$P^{HO_2} = \frac{1}{2}R_6+\frac{1}{2}R_7+R_9+R_{10}+\frac{1}{2}R_{11}+0.94\cdot R_{13}+\frac{1}{2}R_{\underline{25}24}-\frac{1}{2}R_8 \qquad (19)$$

$$L^{HO_2} = 2\cdot R_3+\frac{1}{2}R_4+\frac{1}{2}R_5+\frac{1}{2}R_8+\frac{1}{2}R_{14}+\frac{1}{2}R_{15}+\frac{1}{2}R_{\underline{23}22}+R_{\underline{27}26}+R_{\underline{29}27} \qquad (20)$$

$$\begin{aligned}A^i =& 2\cdot R_2\frac{O_3^i}{O_3}+\frac{1}{2}R_4\frac{O_3^i}{O_3}+\frac{1}{2}R_5\frac{O_3^i}{O_3}+\frac{1}{2}R_{14}\frac{NO_y^i}{NO_y}+R_{\underline{20}19}\frac{NO_y^i}{NO_y}+R_{\underline{21}20}\frac{NO_y^i}{NO_y}\\ &-\frac{1}{2}R_6\frac{O_3^i}{O_3}-\frac{1}{2}R_7\frac{O_3^i}{O_3}-\frac{1}{2}R_{11}\frac{CO^i}{CO}-\frac{1}{2}R_{16}\frac{NO_y^i}{NO_y}-\frac{1}{2}R_{17}\frac{NO_y^i}{NO_y}-\frac{1}{2}R_{\underline{22}21}\frac{NMHC^i}{NMHC}-\frac{1}{2}R_{\underline{25}24}\frac{NMHC^i}{NMHC}\underline{+\frac{resOH}{n}}\end{aligned}\tag{21}$$

$$\begin{aligned}B^i =& \frac{1}{2}R_6\frac{O_3^i}{O_3}+\frac{1}{2}R_7\frac{O_3^i}{O_3}+\frac{1}{2}R_{11}\frac{CO^i}{CO}+R_{18}\frac{NO_y^i}{NO_y}+\frac{1}{2}R_{\underline{24}23}\left(\frac{NMHC^i}{NMHC}+\frac{NO_y^i}{NO_y}\right)+\frac{1}{2}R_{\underline{25}24}\frac{NMHC^i}{NMHC}\\ &+R_{\underline{26}25}\frac{NMHC^i}{NMHC}+R_{\underline{31}28}\frac{NMHC^i}{NMHC}-\frac{1}{2}R_4\frac{O_3^i}{O_3}-\frac{1}{2}R_5\frac{O_3^i}{O_3}-\frac{1}{2}R_{14}\frac{NO_y^i}{NO_y}-\frac{1}{2}R_{15}\frac{NO_y^i}{NO_y}-\frac{1}{2}R_{\underline{23}22}\frac{NMHC^i}{NMHC}\underline{+\frac{resHO_2}{n}+\frac{resH}{n}}\end{aligned}\tag{22}$$

Solving equations (15) and (16), we finally obtain ~~for~~ the contributions of a source category i to the OH and HO_2 concentration (~~compare to Grewe et al. (2017) equations~~ same equations as equations (29) and (30) in Grewe et al. (2017) , but with differently defined coefficients):

$$\frac{OH^i}{OH}=\frac{A^iL^{HO_2}+B^iP^{OH}}{L^{OH}L^{HO_2}-P^{OH}P^{HO_2}}\tag{23}$$

$$\frac{HO_2^i}{HO_2}=\frac{A^iP^{HO_2}+B^iL^{OH}}{L^{OH}L^{HO_2}-P^{OH}P^{HO_2}}\tag{24}$$

These equations are implemented in the TAGGING submodel and EMAC and MECO(n) simulations ~~after~~ according to Sect. 2 are performed. The results for the OH and HO_2 contributions are analysed and compared with V1.0 in the following Section.

4 Results of model simulations

4.1 Contribution of short-lived species (HO_x)

~~Relative differences of the OH contribution obtained by V1.0 towards the further developed HO_x tagging mechanism V1.1. To be consisted, the same year 2010 is taken into consideration.~~

~~Relative differences of the HO_2 contribution obtained by V1.0 towards the further developed HO_x tagging mechanism V1.1. To be consisted, the same year 2010 is taken into consideration.~~

~~Figure~~ Figures 2 and 3 show the zonal mean of ~~the~~ OH and HO_2 contributions up to 200 hPa for the ten source categories ~~up to 200 hPa~~derived by V1.1 (first and third columns) and V1.0 (second and forth columns). The zonal mean of OH and HO_2 contributions from 1 to 200 hPa are shown in ~~the appendix B (Fig~~Appendix B (Figs. B1, B2). First, the OH and HO_2 contributions of V1.1 are described in the following. For the categories which are determined by anthropogenic emissions, such as "shipping", "road traffic" and "anthropogenic non-traffic", the maximum values of OH and HO_2 contributions occur

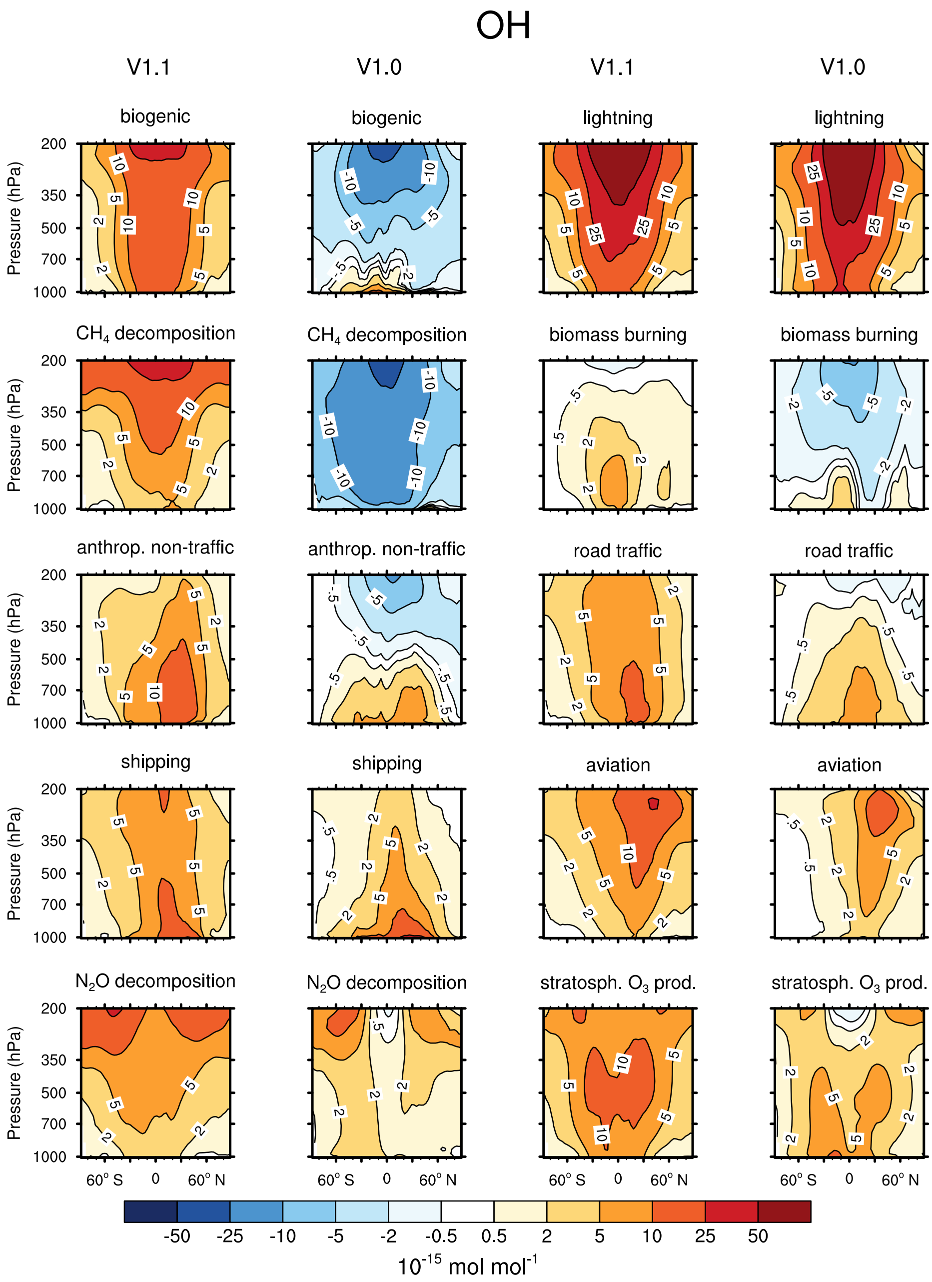

Figure 2. Contribution of ten source categories to OH in 10^{-15} mol mol^{-1}. Zonal ~~mean~~ means of the year ~~2010~~ 2008 are shown. ~~Simluation~~ First and third columns show the tagging method V1.1. Second and forth columns show the tagging method V1.0. Simulation is performed with EMAC.

in the lower troposphere in the Northern Hemisphere. This clearly shows that for ~~the~~ anthropogenic dominated categories the OH and HO_2 contributions are caused by ~~the~~ anthropogenic emissions. The contributions vary among these categories of surface emissions as not only the amount but also the composition of the emissions differs. For the category "aviation", maximum OH contribution are found in the Northern Hemisphere between 200 and 250 hPa. However, HO_2 contribution has a minimum in this region and a maximum in the lower troposphere. The OH values for the categories "CH_4 decomposition", "N_2O decomposition", "lightning" and "biogenic emissions" are largest in the upper troposphere. Most OH contributions of "biomass burning" are found in lower tropical troposphere. In contrast, negative values ~~occurs~~ occur in the upper tropical troposphere. Concerning the HO_2 contribution, the residual categories show a maximum in the tropical lower troposphere. In addition, the category "lightning" shows a strong HO_2 loss in the upper tropical troposphere which is caused by reaction (14).

The results obtained ~~in this study~~ by V1.1 are compared to the OH and HO_2 zonal profiles of V1.0 only in the troposphere ~~up to 200 hPa.~~(Figs. 2 and 3). The HO_x tagging ~~mechanism~~ method V1.0 was only developed for the troposphere. Hence, a comparison in the stratosphere ~~would not be reasonable. The relative differences of V1.0 towards V1.1 for the year 2010 are shown in Fig. ?? and ??.~~ is not reasonable. In general, contributions to OH and HO_2 concentrations of V1.1 are larger in the ~~free troposphere and smaller in the boundary layer~~ troposphere compared to V1.0. ~~Also, the HO_2 contributions show a large increase over the whole troposphere. This overall shifts~~ This overall shift towards larger values ~~can be~~ is explained by the ~~introduction of the rest terms: For each of the ten source category a tenth of the rest term is added to the OH and HO_2 contributions, which leads to larger values compared to~~ re-establishment of the steady-state and thus the closure of the budget in V1~~.0.~~

~~V1.0 overestimated the contributions to OH in the boundary layer because only a few OH loss reactions were considered. The addition of new OH loss reactions such as reaction (10) cause a lower contributions to OH in V1~~.1. ~~Moreover,~~ In V1.0 ~~indirectly calculated the rate of reaction (22) by the production of CO. In comparison, V1.1 directly calculates the rate by including all reactions with NMHC (see Sect. 3.4). This also affects the change of OH contribution in the boundary layer.~~ the budget was not closed and thus the contributions were underestimated.

For OH, the categories "lightning" ~~, "shipping"~~ and "aviation" show no large changes in the general pattern of the zonal means ~~. The categories "anthropogenic non-traffic", "road traffic", "N_2O decomposition" and "stratospheric O_3 production" showed an OH loss in the upper tropical troposphere in~~ between V1.0 ~~which is not visible in~~ and V1.1~~anymore.~~

~~The "biomass burning" category shows large changes in pattern. The OH contributions strongly decreases in the upper and increases in the lower troposphere. Many new reactions of NMHC are added in V1.1~~. ~~These reactions as well as the better representation of reaction rate (22) are responsible for the decrease of the minimum in the upper troposphere.~~

~~Major~~ Considering the HO_2 contributions, no large changes are found ~~in~~ for the categories "~~CH_4 decomposition~~biomass burning" ~~and~~ , "~~biogenic emissions~~anthropogenic non-traffic"~~. The OH contribution of both categories in V1.0 was negative over the whole atmosphere with a strong OH loss in the upper tropical troposphere. In V1.1, the patterns switch their signs: the contributions are positive with a maximum in the upper tropical troposphere. In both categories, NMHC are dominating. The reactions of NMHC with OH, HO_2 and NO_y (reaction 22~~, ~~23 and 24) are important throughout the whole troposphere. V1.0~~

~~did not consider all reactions of NMHC with OH, HO_2 and NO_y (see Sect. 3.4). Now, V1.1 regards all reactions of OH, HO_2 and NO_y with NMHC. This causes large changes in pattern.~~ "road traffic" and "shipping".

~~Considering the HO_2 contributions, no large changes in the general zonal pattern are found in the categories "biomass burning", "anthropogenic non-traffic", "road traffic" and "shipping". Large changes in pattern occur for the~~ The contribution of the category "~~biogenic emissions~~aviation" ~~and "CH_4 decomposition". Especially in the lower troposphere,~~ to HO_2 in V1~~.0 showed a rather ragged structure while~~ .1 shows roughly the same pattern compared to V1.0. However, the HO_2 destruction along the flight path is not as pronounced any more which is caused by the inclusion of reaction (15) and (18) to V1.1~~presents a smooth pattern. No negative values occur anymore. Many new reactions are now considered in the~~ . Reaction (15) adds the term $\frac{1}{2}R_{15}\frac{NO_y^i}{NO_y}$ to the HO_2 loss (eq. 12) and reaction (18) adds the term $R_{18}\frac{NO_y^i}{NO_y}$ to the HO~~$_x$ tagging mechanism and thus contribute to pattern changes. In particular for "CH_4 decomposition", the consideration of further reactions of NMHC producing HO~~$_2$ production (eq. 11). As reaction rate R_{15} equals the rate R_{18}, this leads to a larger HO_2 production than HO_2 loss $\left(R_{18}\frac{NO_y^i}{NO_y} > \frac{1}{2}R_{15}\frac{NO_y^i}{NO_y}\right)$. Consequently, the addition of reaction (15) and (~~reaction 25 and 26) largely contributes to the pattern change in HO~~18) to the reduced HO_x reaction system V1.1 constitutes an extra HO_2 source.

~~The larger values of~~ Larger values of the categories "N_2O decomposition" and "lightning" to HO_2 in the upper troposphere ~~can be explained by several effects. Amongst others, the introduced H tagging contributes~~ are explained by a larger HO_2 production in V1.1 compared to V1.0. The H tagging in V1.1 considers all relevant HO_2 sources (reaction (7), (10), (11) and (28)) leading to a larger HO_2 production. ~~Furthermore, mostly NO_y emissions contribute to the~~ Also the addition of reactions (15) and (18) (explanation see above) as well as the addition of reaction (23) which considers more reactions than in V1.0 increase the HO_2 contribution of the categories "N_2O decomposition" and "lightning". ~~V1.1 regards many new reactions concerning NO_y. In particular, the photolysis of HONO and HNO_3 increases regionally the OH production. Via equation (24) the addition of these reactions also causes the HO_2 increase in the upper troposphere.~~

~~The category~~

Large changes in pattern are observed for the contributions of "~~aviation~~biogenic emissions" and "~~shows roughly the same pattern compared to V1.0. However, the~~ CH_4 decomposition" to OH and HO_2 ~~destruction in the flight path is not as pronounced any more. The sector~~ as well as for the contributions of "~~aviation~~biomass burning" ~~is dominated by NO_y emissions. Considering reaction (18)~~ and "anthropogenic non-traffic" to OH. In V1.1, these categories mainly constitute a source of OH and HO_2 in the troposphere. The addition of reaction (24) and (25) to the reduced HO_x reaction system V1.1 ~~adds an extra~~ presents a HO_2 source ~~to this region. Thus the minimum is not as pronounced in V1.1 compared~~ increasing OH and HO_2 contributions. Furthermore, reactions of NMHC with OH, HO_2 and NO_y (reaction 21, 22 and 23) are important throughout the whole troposphere. In contrast to V1.0.

~~The same effect can be seen in categories~~ , V1.1 considers all reactions of NMHC with OH, HO_2 and NO_y (see Sect. 3.2) significantly changing the pattern of "~~road traffic~~biogenic emissions", "~~shipping~~CH_4 decomposition", "biomass burning" and "anthropogenic non-traffic". ~~In the boundary layer at 40-60° N, V1.0 had a HO_2 minimum. The consideration of reaction (18) adds an extra HO_2 source and thus dissolves the alleged HO_2 reduction of V1.0.~~

To quantify the impact of the advanced HO_x tagging ~~mechanism~~ method on regional scale, Fig. 4 shows the contributions of ship emissions to OH and HO_2 in the boundary layer simulated with the high resolution model MECO(n) (see Sect. 2). The ship paths in the Atlantic, Mediterranean and Red Sea are clearly visible and lead to OH and HO_2 production along these paths. In the polluted area at the coast of Marseille the OH and HO_2 contributions are reduced, although NO_y from shipping emission is larger than in the Mediterranean Sea. However, O_3 from shipping is also larger in this region. This ~~can cause stronger~~ causes a larger HO_2 and OH loss via reaction (4) and (6) than in the Mediterranean Sea.

The tagging ~~mechanism~~ method V1.0 (Grewe et al. (2017) their Fig. 6) showed negative HO_2 shipping contribution along the ship paths. This ~~could be~~ was explained by reaction (14): NO destroys HO_2 and leads to negative contributions. However, in V1.1 HO_2 shipping contributions are positive. The ~~contribution of ships to NO_y is very large. Thus,~~ change of sign is caused by the addition of reaction (15) and (18) ~~causes the change of sign. Although, the reaction rate R_{15} equals the rate R_{18}, more HO_2 is produced by ships than is destroyed: only half of the HO_2 which is destroyed by reaction (15) is added to the~~ to the reduced HO_x reaction system V1.1 which constitutes a net HO_2 ~~destruction per category $LossHO_2^i$ (eq. 12). In contrast, all HO_2 which is produced by reaction (18) is added to the~~ production leading to positive HO_2 ~~production per category $ProdHO_2^i$ (eq. 11). As more~~ contributions (explanation see above). The comparison shows that HO_2 ~~of the shipping sector is produced than destroyed, a shift to positive values is caused.~~ contributions in V1.0 were systematically and erroneously underestimated.

To summarize, the contributions to OH and HO_2 concentrations show larger values in V1.1 compared to V1.0. This ~~can be~~ is explained by the ~~introduction of the rest terms~~re-establishment of the steady-state. For OH, no large changes are found in the categories "lightning" ~~, "shipping"~~ and "aviation". However, large changes are found for "biomass burning", "CH_4 decomposition" and "biogenic emissions". For HO_2, no large differences occur in the categories "biomass burning", "anthropogenic non-traffic", "road traffic" and "shipping". In comparison, the categories "biogenic emissions" and "CH_4 decomposition" differ strongly. The differences between the contributions of V1.1 and V1.0 ~~can be~~ are traced back to the addition of certain reactions to the reduced reaction system considered in the HO_x tagging ~~mechanism~~method.

4.2 Effects on long-lived species

The ~~changes of HO_x contributions feed backs~~ tagging of short-lived and long-lived species closely intertwine (see Fig. 1). Changes in the contributions to OH and HO_2 influence the contributions to the long-lived ~~tracer~~ tracers O_3, NO_y, CO, NMHC and PAN. ~~Exemplary~~For example, Figure 5 shows the ~~O_3 zonal mean for the~~ zonal mean of the contributions of the ten source categories to O_3. Grewe et al. (2017) presents the same figure for the ~~their~~ HO_x tagging ~~mechanism~~ method V1.0 (their Fig. 4). For consistency, we compare our results with the results of Grewe et al. (2017) only for the year ~~2010.~~ 2008.

In general, no large differences between V1.1 and V1.0 for long-lived species are found. The category "biogenic emissions" and "CH_4 decomposition" show an O_3 increase in the tropical troposphere. "Stratospheric O_3 production" slightly increases in the Southern Hemisphere. Small O_3 changes are found for the categories "~~lighting~~lightning" ~~, "biomass burning", "road traffic"~~ and "N_2O decomposition". Regarding the ~~other~~ remaining long-lived species ~~, CO from~~ (see Figures S3 – S6 in the Supplement), the contribution of "~~biogenic emissions~~biomass burning" ~~and~~ to CO decreases while the contributions of "~~CH_4 decomposition" decreases while CO from~~ biogenic emissions" ~~lighting"~~ to CO increases in the Southern Hemisphere. The remaining sectors stay rather unchanged. ~~Only the sectors "lighting", "CH_4 decomposition", "biomass burning" and "road traffic" vary little for PAN.~~ NO_y~~and NMHC~~ , NMHC and PAN show only minor changes. Even though, major differences in OH and HO_2 occur between V1.0 and V1.1, these do not have a large effect on the long-lived species.

5 Discussion and Conclusion

We present an extension of the HO_x tagging ~~mechanism~~ method described by Grewe et al. (2017). 15 new reactions producing and destroying HO_x are added to tagging meachnism. In Grewe et al. (2017), the HO_x tagging ~~mechanism~~ method V1.0 was restricted to the troposphere only. We further include the reactions which are essential for HO_x production and loss in the stratosphere. ~~In particular the production of HO_2 by H and O_2 and the reaction of OH and HO_2 with O(^{3}P) are important in the stratosphere and are now taken into account.~~ Moreover, we introduce an equivalent tagging ~~mechanism~~ method to obtain the contributions to the H radical. This step is mandatory to fully account for the main HO_2 source: the reaction of H with O_2.

In V1.0, the ~~budget of~~ steady-state assumption was not completely fulfilled resulting in an unclosed budget: the sum of the HO_x contributions and the total HO_x concentration deviated by ~~ca.~~ about 70 %. ~~The addition of 15 new reactions to the reaction system leads to a better closure (deviation of 25). However, since we have to omit certain reactions from the tagging mechanism, the production and loss rates are less balanced. Since this is a crucial assumption for the~~ To re-establish steady-state, we add more reactions to the reduced HO_x ~~tagging mechanism, we explicitly~~ reaction system and introduce rest terms to balance the deviation of HO_x production and loss. ~~The rest terms are equally distributed over the source categories.~~ This leads to the closure of the budget. Thus, the tagging meachnism introduced by Grewe et al. (2010) operates not only for long-lived but also for short-lived species.

The advanced HO_x tagging ~~mechanism~~ method V1.1 was implemented in ~~a global climate-chemistry~~ the global chemistry climate model EMAC and in ~~a~~ the regional model MECO(n). A 1-year simulation was performed in both model systems and compared to V1.0. ~~The categories"lightning", "shipping" and "aviation" show no large changes in OH zonal pattern. Major changes in OH contributions are found in "biomass burning"~~For most categories, the general zonal pattern of the contributions to OH and HO_2 show minor differences. In contrast, large changes are observed in the category "~~CH_4 decomposition" and "~~biogenic emissions" ~~. The HO_2 zonal pattern of the categories "biomass burning", "anthropogenic non-traffic", "road traffic"~~ and "~~ship" do not differ from V1.0. However, the categories "N_2O~~ CH_4 decomposition" ~~, "lightning" and "aviation" show some changes which could be~~ which are traced back to the addition of ~~individual reactions to the tagging mechanism. In general, an overall shift towards larger values is found in all categories which is caused by the rest terms. Little changes are found in NO~~certain reactions to V1.1. Although the contributions of long-lived and short-lived species influence each other, no large changes are found for long-lived species.

The mechanism presented in this study (and introduced by Tsati (2014) and Grewe et al. (2017)) is the first method for tagging short-lived species. Other studies quantify the source attributions of chemical species with a significant longer lifetime. The idea of source attribution is applied to attribute CO to different emission types and regions (e.g. **???**) , to attribute NO_x concentrations to emission sources (**?**) or to trace stable isotopic compositions (**?**) . Also for the source attribution of tropospheric O_3, several tagging approaches exist attributing tropospheric O_3 only to NO_x sources (**??**Grewe et al., 2012; **?**) , only to NMHC sources (**??**) or to NO_y, ~~NMHC and PAN~~CO and NMHC emissions simultaneously (Grewe et al., 2017) .

A common technique to quantify the impact of emissions to OH is the so called perturbation method which compares two simulations: one simulation with all emissions and one simulation with reduced emissions (e.g. **??**) . However, ~~O_3 presents certain changes in the tropical troposphere for the categories "biogenic emissions" and "CH_4 decomposition". Furthermore, CO shows some variations in the categories "biogenic emissions", "CH_4 decomposition" and "lightning"~~if the underlying chemical processes are non-linear (as it is the case for OH), the perturbation method largely underestimates the contribution (Grewe et al., 2012; **?**; **?**) . Consequently, the tagging approach presented in this study delivers the actual contribution of the emission source while the perturbation method displays the impact of the emission reduction.

~~The~~ To conclude, the further developed HO_x tagging method can be used to identify the ~~effect~~ contribution of anthropogenic emissions on the atmospheric composition. In particular, the contribution of emission sectors on the concentrations of OH and HO_2 in the troposphere and stratosphere can be achieved. This method will be applied for re-evaluating the impact of the traffic sector on ~~the~~ climate.

Code availability. The Modular Earth Submodel System (MESSy) is continuously further developed and applied by a consortium of institutions. The usage of MESSy and access to the source code is licensed to all affiliates of institutions, which are members of the MESSy Consortium. Institutions can become a member of the MESSy Consortium by signing the MESSy Memorandum of Understanding. More information can be found on the MESSy Consortium Web-site (http://www.messy-interface.org). The submodel TAGGING 1.1 will be included in MESSy version 2.54. The code being used to obtain the presented results is available upon personal request.

Appendix A: Exclusion of reactions from reduced HO_x reaction system V1.1

The annual mean reaction rates of the following three reactions are also greater than $10^{-15}\,\mathrm{mol\,mol^{-1}s^{-1}}$ and thus would usually be accounted to the reduced HO_x reaction system V1.1:

$$H_2O_2 + h\nu \longrightarrow 2OH \tag{A1}$$

$$HOCl + h\nu \longrightarrow OH + Cl \tag{A2}$$

$$HOBr + h\nu \longrightarrow OH + Br \tag{A3}$$

However, the tagging method can not be applied for these three reactions.

To include the OH production by the photolysis of H_2O_2 (reaction A1), we would need to tag H_2O_2. Since the production and the loss of H_2O_2 are not balanced, we can not assume a steady-state. Thus, a similar tagging approach as for HO_x and H is not valid for H_2O_2. Consequently, we exclude the reaction (A1) from the HO_x tagging method. This reaction contributes about 8 % to the total OH production in the troposphere.

Hypochlorous acid (HOCl) and hypobromous acid (HOBr) are photolysed in the stratosphere and produce OH (reaction A2 and A3), but HOCl and HOBr are not tagged. Although the steady-state assumption is globally valid, locally the production and loss of HOCl and HOBr are not balanced everywhere. In the stratosphere, for about 65 % of the model grid boxes the production deviates by more than 10 % from the loss of HOCl and HOBr. In particular, in the transition area between day and night in the polar region, the production deviates strongly from the loss. Also at night where the reactions mostly occur, the steady-state is not fulfilled everywhere. Moreover, since both species are not radicals, their lifetimes can not be assumed to be short. Hence, we can not apply the tagging method, so we have to omit the reactions (A2) and (A3) from the reduced HOx reaction system V1.1.

Considering reactions (A1), (A2) and (A3) to the reduced HO_x reaction system V1.1 would lead to a significantly larger OH production in the troposphere representing about 98 % of the total OH production rate derived by MECCA. In the stratosphere, 91 % of the total OH production would be regarded. Hence, excluding these reactions from the reduced HO_x reaction system V1.1 worsen the steady-state assumption between OH production and loss. The rest term *resOH* introduced in Sect. 3.4 compensates this deviation from production and loss rate.

Appendix B: HO_x contributions in the stratosphere

~~Fig~~Figs. B1 and B2 show the zonal mean of OH and HO_2 from 1 to 200 hPa. ~~Note the logarithmic scale of the contour levels.~~ As OH concentration strongly ~~raises~~ rises with increasing height, so do the contributions to OH. The category ~~“biomass burning”~~ "biomass burning" shows negative OH values in the tropopause region. In this region, also large CO values from ~~“biomass burning”~~ "biomass burning" occur. CO effectively destroys OH by reaction (11) which causes this OH loss. The large ~~negative minimum~~ OH loss in the lower stratosphere of the category "stratospheric O_3 production" is mainly caused by the destruction of OH by O_3 (reaction 6).

The contributions ~~of all categories~~ to HO_2 in the stratosphere increases with height as well. The categories ~~“biogenic emissions”, “lightning”, “biomass burning”, “~~"biogenic emissions", "lightning", "biomass burning", "anthropogenic non-traffic~~”, “road traffic”, “shipping” and “aviation”~~", "road traffic", "shipping" and "aviation" show a local maximum at around 5~~hPa. Negative values occur in tropopause region for~~ hPa which is caused by omitting the photolysis of HOCl (see Appendix A).

For the category "lightning"~~. This is induced by large values of NO_y which mostly destroy~~ , HO_2 is destroyed by reaction (14) in the tropopause region. The category ~~“~~"N_2O decomposition~~”~~" shows negative values in the lower stratosphere and a strong negative minimum at around 10 hPa which is also caused by reaction (14). The local maximum with positive HO_2 contributions indicates that in this region the HO_2 production via reaction (1) and (6) dominates the HO_2 loss via reaction (14).

Competing interests. There are no competing interests.

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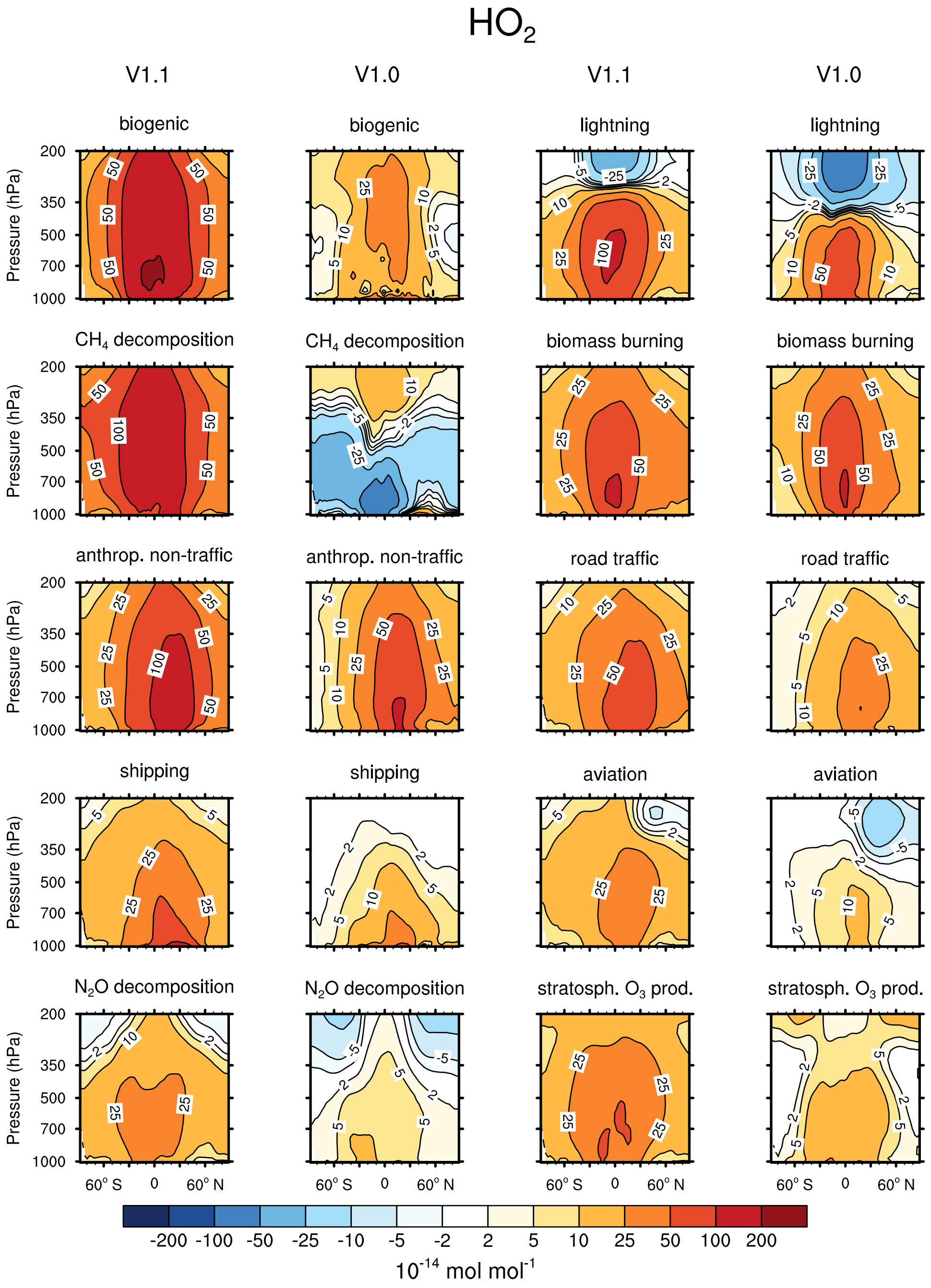

Figure 3. Contribution of ten source categories to HO_2 in 10^{-15} mol mol^{-1}. Zonal ~~mean~~ means of the year ~~2010~~ 2008 are shown. ~~Simluation~~ First and third columns show the tagging method V1.1. Second and forth columns show the tagging method V1.0. Simulation is performed with EMAC.

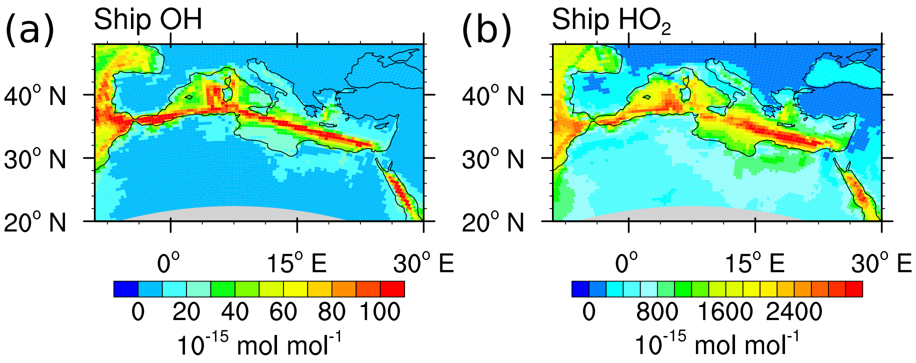

Figure 4. Contribution of shipping emissions to OH and HO_2 in 10^{-15} mol mol^{-1}. Monthly ~~mean~~ means of ground level values in August 2007 are shown. ~~Simluation~~ Simulation is performed with MECO(n).

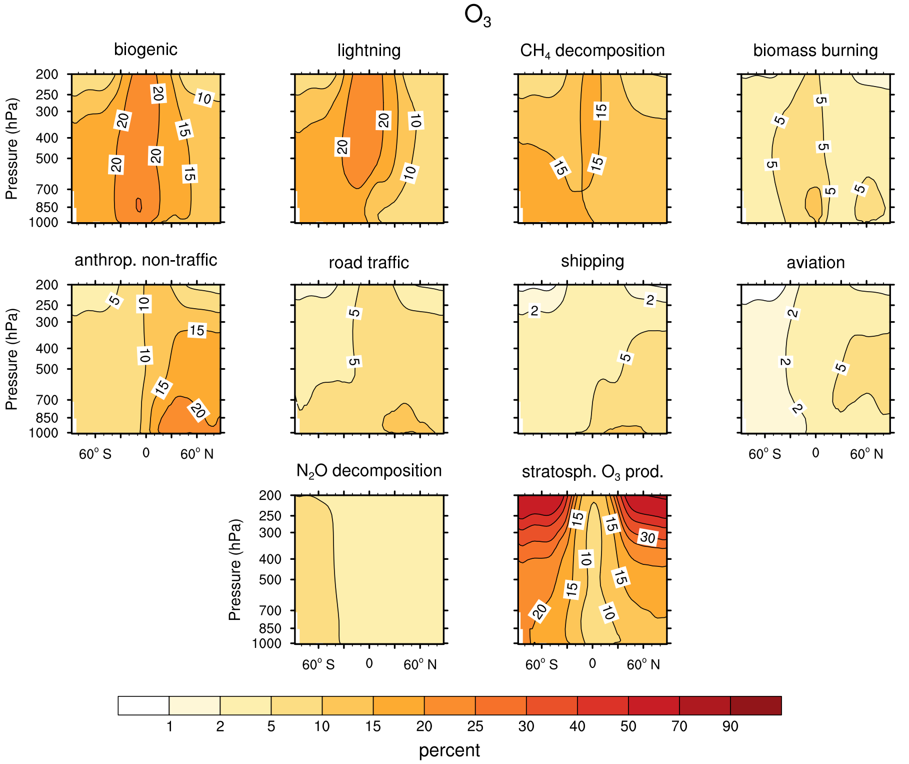

Figure 5. Annual mean ~~contribution~~ contributions of ten source categories to O_3 concentration in %.

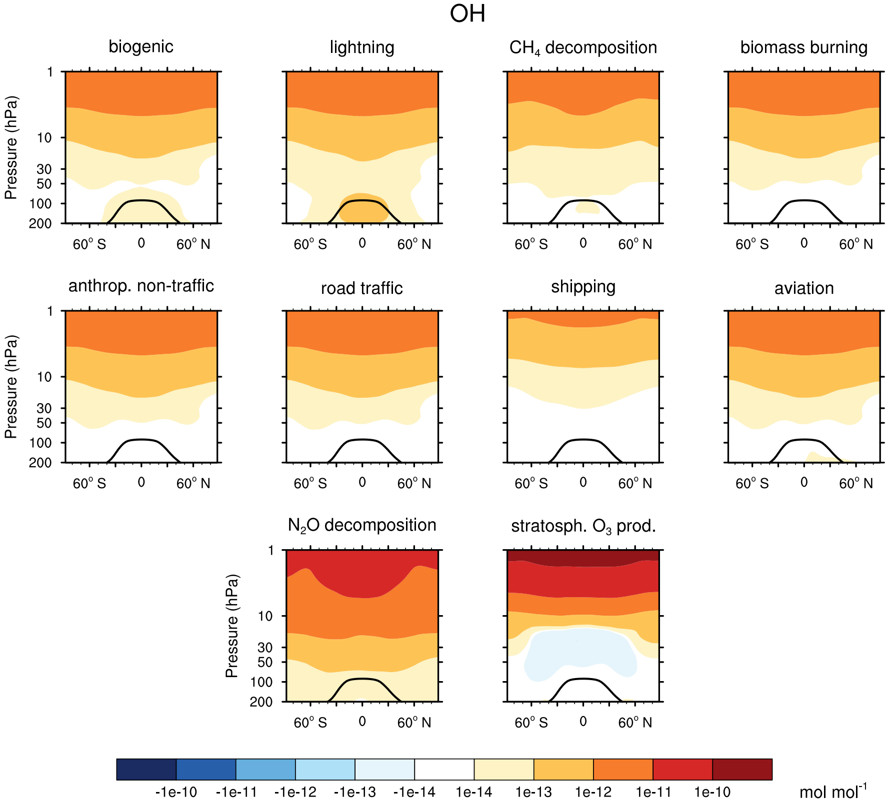

Figure B1. ~~Contribution~~ Contributions of ten source categories to OH in the stratosphere. Zonal ~~mean~~ means of the year 2010 are shown. Black line indicates the tropopause. ~~Simluation~~ Simulation is performed with EMAC. Note the logarithmic scale of the contour levels.

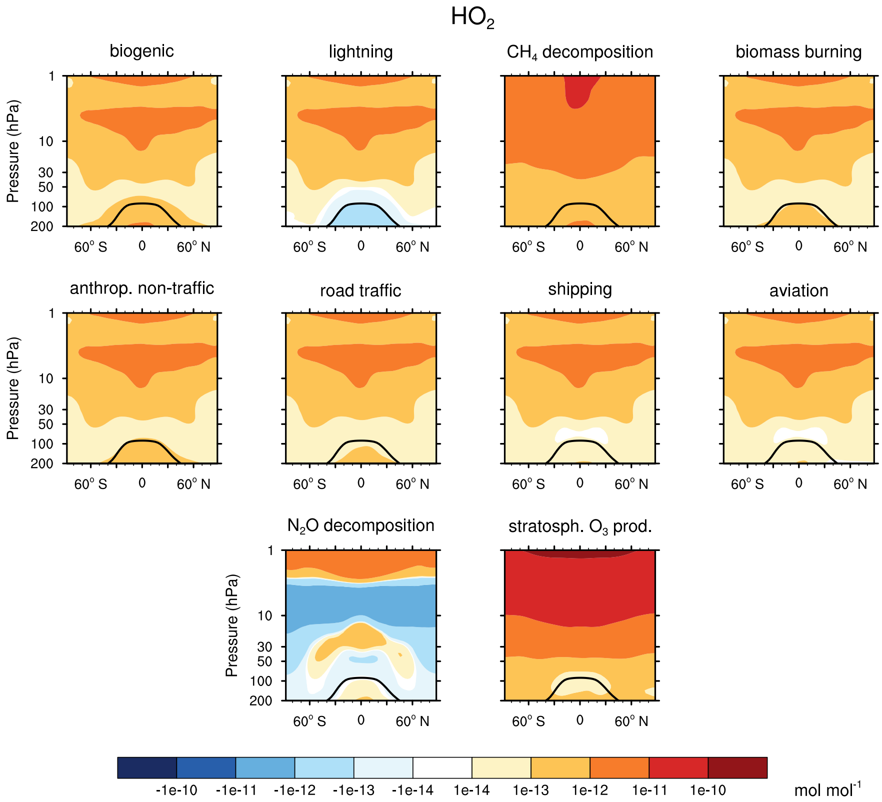

Figure B2. ~~Contribution~~ Contributions of ten source categories to HO_2 in the stratosphere. Zonal ~~mean~~ means of the year 2010 are shown. Black line indicates the tropopause. ~~Simluation~~ Simulation is performed with EMAC. Note the logarithmic scale of the contour levels.