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Interactive comment on "Effects of heterogeneous reactions on global tropospheric chemistry" *by* Phuc T. M. Ha et al.

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Dear Anonymous Referee #2, We appreciate your time and effort dedicated to providing valuable feedback on our manuscript.

Referee's comment: This manuscript presents a global model-based study of the impacts of various heterogeneous uptake processes on tropospheric composition. The CHASER model is validated against a number of ground-, ship-, aircraft-, and satellite-based observations of relevant species (NOx, PM, O3, CO, OH, and total column O3) and parameters (cloud fraction). A variety of simulations are designed to probe aerosol, cloud droplet, and ice particle uptake of N2O5, HO2, and RO2, with individual species and uptake pathways (cloud versus aerosol) turned off in turn. Total

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and spatially-/temporally-resolved changes in methane lifetime, NOx, O3, and CO are assessed. Finally, a sensitivity simulation is conducted to evaluate the impacts to atmospheric composition with variations in the examined heterogeneous loss rates. The study presents a well-rounded analysis of heterogeneous uptake from a global model perspective. The model is thoroughly assessed against a reasonable number of available observations. The thoroughness of sensitivity simulations, both turning on/off all and individual heterogeneous uptake reactions as well as varying the magnitude of the first-order loss rate applied, addresses in a methodical way how this chemistry might impact global composition. I think there may be a missed opportunity in this manuscript to more thoroughly discuss the mechanisms through which these impacts manifest, but diagnostics necessary to perform such assessments may be lacking, and this should not preclude publication of this work. There is also a concern that model biases (such as the overestimation in cloud fraction in the northern Pacific lower troposphere) will introduce model-dependent errors in the results, though I regard the acknowledgment of this issue in the text as sufficient. I would consider this work as suitable for publication in this journal following the incorporation of the suggestions noted below, primarily concerned with clarifications and organization.

Author's response: We are grateful to Reviewer # 2 for the insightful and positive comments on our manuscripts. We thank you for recognizing some deficiencies of the current manuscript relates to model-dependent errors, e.g. overestimation of the model CHASER against the low troposphere cloud for the North Pacific region, and the opportunity for in-depth discussions of the mechanisms involved in the effects of heterogeneous reactions. We also thank Reviewer #2 for understanding our acceptable coverage of these shortcomings. We have been able to incorporate changes to reflect most of the suggestions provided by Reviewer #2.

Referee's comment: Major comment 1. In addition to collective improvements to figure clarity and organization, noted below under minor comments, my only other major request would be to expand on discussions of the mechanisms underlying some of the

changes exhibited in the presented results. For instance, the description of effects on PAN production and transport, L492, could be more explicit and re-emphasized in the Conclusions.

The reasons for the large increases in NOx near the surface in the Arctic during JJA due to HR(RO2) are still unclear to me – if there were a large source of NOx here, the reduction in PAN formation may make sense, but large sources at these high latitudes seems unlikely.

Similarly, why are there increases in NOx during DJF due to HR(RO2) in the high latitude southern oceans, just offshore?

Author's response: L543-L548: For the Arctic ocean during JJA, large increases in NOx near the surface are due to the reduction of PAN caused by HR(RO2), as described in the current manuscript, in association with the suppress for NO oxidation via (R11) which is described in the revised version. These two reasons resulted in the double increase for NOx by HR(RO2) (144%) as compared to that by HR(HO2) (66%). (R11) RO2 + NO $\rightarrow$ RO + NO2

The NOx increases in DJF at high latitudes of southern oceans' offshore could also relate to reduced transport of NOx due to reduced PAN formation since these offshores are in the downwind areas of major BVOCs sources from South America, South Africa, and Australia. Moreover, the areas with significant NOx increases in Fig. 12 (right panels) are all linked with high-cloud SAD (Fig. S14 left panels). The additional discussion was added accordingly.

L670-672: We also added discussions on HR(RO2) effects in the conclusion, regarding its effects on PAN and NOx transportations and the reducing effect on CO.

Referee's comment: Major comment 2. Similarly, one impact attributed to RO2 uptake is a decrease in CO (e.g., L257). I'm curious about the mechanism, and not aware of any discussion regarding this. I would assume that the CO decrease is due sim-

ply to reductions in secondary production – functionalized C-containing RO2 species that would otherwise be oxidized to form CO are instead taken up on aerosols/cloud droplets. Do the authors know if this is the case, or if there is another mechanism at play? I understand that diagnosing these kinds of questions from global model output, especially from lengthy and numerous simulations, may be difficult, given limitations on how much output can be generated. While model evidence to further describe these mechanistic questions would be ideal, hypotheses supported from prior literature or simpler, logical arguments would suffice.

Author's response: L561-564: We agree that there is a lack of discussion on the CO's decreasing impact due to HR(RO2), which differs from the increasing impacts due to HR(N2O5) and HR(HO2). As advised by the Referee, CO decrease might be due to reduction in CO's secondary production from oxidation of functionalized RO2 species (RO2 → HCHO/RCHO or ROOH → CO) such as isoprene (Kelvin and Jacob, Atmos. Chem. Phys., 19, 9613–9640, 2019) when these RO2 species undergo instead the heterogeneous reactions on aerosols and clouds particles.

Minor comments: Referee's comment: L120: Please add a reference for the MAC reanalysis biomass burning emissions, or else provide more detail

Author's response: L121: Reference for the MACC reanalysis system was added (Inness et al., 2013).

Referee's comment: L175: Somewhere in Section 2, the timeframe of the simulations should be clearly stated. I gather from some of the time series figures that model output is available for at least 2010-2018 – were all sensitivity simulations run for this entire period?

Author's response: L180: All the standard and sensitivity runs were conducted in the 2009-2017 timeframe, using 2009 for the spin-up year. We added a sentence regarding the simulation timeframe.

Referee's comment: L255: The discussion surrounding Fig. 3 refers to differences between the various model sensitivity runs, but it is very difficult to make out the different colored lines representing the different simulations in the figure. Perhaps an inset that shows a "zoomed in" view of a representative portion of each panel, or else plotting in different coordinates, like % difference compared to obs versus time, would help remedy the issue. This applies to Figures 4 and 5 as well.

Author's response: L285: We removed the coloured lines representing sensitivity runs and keep only observation (grey), noHR (black) and STD simulations (red) in Fig. 3, to better focus on the overall improvement of the model with HRs inclusion. Additional plots for heterogeneous effects on NOx, O3, CO caused by each HR were added to Fig. 3 to support the discussion on the different HR effects. Similar modifications were applied to Fig. 4 and 5 as well. Fig. 1, Fig. 6, Fig. 9 to 14, Fig. S15, S16 were also changed for better visualization.

Referee's comment: L286: The suggestion of insufficient downward mixing of stratospheric air in the model while CO is underestimated by the model seems counterintuitive to me. Stratospheric air should be depleted in CO, so I would expect higher observed CO would point to something other than stratospheric influence, especially at the surface, as the shipbased observations are. I'm unfamiliar with Kanaya et al.; do they provide some other rationale to explain this apparent discrepancy?

Author's response: L318-322: We agree that the suggestion of insufficient downward mixing of stratospheric air in the model could only explain the underestimates by the model for O3 in NP and Arctic regions (Fig. 4 b: T1, T4, T5, T6). Model's underestimation for CO in the same region (< 30 ppbv) should be explained by insufficient emissions for CO as we used the HTAP-II inventory, as the CO biases are only minor in Kanaya et al. (2019) which used reanalysis data by inverse modelling as emission input to CHASER. In the revised manuscript, we modified the reason for CO's underestimation by model as insufficient emissions for CO.

Referee's comment: L334: It is unclear to me why the "ground layer" is defined differently for all flights (> 800 hPa) versus for the N. Pacific region (> 700 hPa) in Table 8 – could the authors include a brief explanation?

Author's comments: L376-377: We agree that the given sentence was unclear. The base idea is that "HR(HO2) seems only to reduce the model bias in a thin layer: from the ground up to 800 hPa for all flights and 700 hPa for the North Pacific region ", the sentence will be modified as above.

Referee's comment: L365: I feel that the TCO plots in Fig. 7 would be more easily understood by plotting Model – OMI differences, for both the STD and noHR simulations. As is, the differences between the model runs and OMI stand out far more than the differences between the STD and noHR runs. One really has to focus on small details to see where the model is improving with respect to OMI.

Author's comments: L420: Thank you for the suggestion. We exchanged the original Fig. 7 with the plots of STD – OMI and noHR – OMI differences for TCO.

Referee's comment: L466: The statement that "recent O3 increases can be attributed to reduced HO2 uptake under aerosol (PM) decreases brought about by the new Chinese Air Pollution policy," is, I think, too strongly worded without a quantitative accounting of the observed O3 changes. Other effects, such as the non-linearity in O3 production with NOx concentration, could also be contributing. Qualifying the statement as "can be attributed in part to reduced HO2. . ." or similar, would be sufficient.

Author's response: L514: The text was modified as " the observed recent O3 increases can be attributed in part to reduced HO2 uptake under aerosol (PM) decreases brought about by the new Chinese Air Pollution policy.".

Referee's comment: L548: "magnitude of HRs" is vague; could you clarify if this sensitivity test is meant to probe uncertainties in the first-order loss rate, possible non-linearities in the uptake, etc.?

Author's response: L620: The sensitivity test is meant to test the effective-oxidation sensitivity of the troposphere in case future pollution and climate change might enhance the activities of these HRs, e.g. enhance the surface aerosol density Aj in Eq. (8). In other words, this test is not meant to probe the uncertainties in the first-order loss rate but meant to probe the possible non-linearities in the response of tropospheric oxidation capacity to the linear enhancement of the loss rate, due to the complexation of tropospheric chemistry. Thus we modified the phrase "magnitude of HRs" to "magnitude of loss rate".

Referee's comment: L589: I'd suggest staying consistent with the number of significant figures reported in the % changes here, in the abstract (L13), and elsewhere. Sometimes one digit is reported after the decimal place, sometimes two, and sometimes none.

Author's response: L14: We have modified the figure followed by % change, with two decimal places for global average changes, and no decimal places for changes at the regional level (e.g. North region Pacific or China).

Referee's comment: Figs. 10 and 14: x-axis labels would be helpful, for anyone who may miss the (%) in the title.

Author's response: x-axis labels with unit % were added into Figs. 10 and 14 (Fig. 14 was updated as Fig. 13).

Referee's comment: technical corrections. L130: "uncertainties" should be "uncertain" (→ L131) L293: "undervalues" is a slightly out-of-place word choice; "underestimates" may be better (→ L328) L297: The use of "extends" here suggests that model underestimates are extending in time/space instead of getting worse. "worsens" or "exaggerates" may better reflect the intended meaning. (→ L332) L301: A verb is needed in this sentence; "Ocean is mostly dominated. . ." (→ L336) L325: "However, for the. . ." the "for" is not needed. (→ L368) L326: Here and elsewhere, I'd suggest the authors check for consistency in how "ATom1" is capitalized and punctuated. (→L369) L364:

The order of appearance of the Supplemental figures should match the order in which they are mentioned in the main text. (→ L410) L380: “surface aerosol density” should be “surface area density” (→ L426) L415: “preferably onto” confuses the meaning of this sentence; I suggest “rather than onto” to emphasize the importance of aerosol uptake over cloud uptake (→ L461) L503: “glob” should be “globe” (→ L573) L502: Fig. 14 is introduced here before Fig. 13 is discussed; I’d suggest switching the two. (→ L572)

Author’s response: All modifications are made as suggested, highlighted in the respective lines.

Referee’s comment: L536: The phrase “N2O5 uptake on aerosols are mostly ascribed” would be more easily understood as “N2O5 uptake is mostly ascribed to aerosols”

Author’s response: L606: The meaning is not only “N2O5 uptake is mostly ascribed to aerosols” in the mid and upper troposphere, but also the aerosols N2O5 uptake is the most dominant HRs in these atmospheric layers. So we change it to “the N2O5 uptake on aerosols is dominant in these layers”.

Sincerely,

On behalf of all co-authors, Phuc T. M. Ha.

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