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Geoscientific Model Development Discussions
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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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Response to Anonymous Referee #1's comment, We thank the Anonymous Referee for the thorough comments on our manuscript.

Referee's comment: This paper evaluated the effects of heterogeneous uptake reactions of N2O5, HO2 and RO2 on cloud and aerosol particles by using a chemical-climate model CHASER, and the modelling results have been verified by comparing with ground-based measurements, shipboard, aircraft and satellite observations. Although the findings of this study on the changes in global abundances of NO2, NO3, O3, and CO, and lifetime of CH4 are basically within the range of uncertainties of previous studies, and no new surprising finding are reported, this work provides the



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most comprehensive view among this kind of studies covering the lower to upper troposphere, polluted terrestrial and remote oceanic region, and seasonal to annual characteristics. Particularly the study demonstrated the heterogeneous effect in the remote areas such as oceanic region and the upper troposphere for the first time. Tthe present reviewer judges this paper is acceptable for publication after considering the following comments.

Author's response: We genuinely appreciated the productive comments from Referee #1 for our work.

Referee's comment: 1. The difference between the role of uptake of HO2 and RO2 should be explained more in detail. In the case of the uptake of RO2, the reduction of the formation of PAN and organic nitrates due to the reactions, CH3COO2 + NO2 → PAN, and RO2 + NO → RONO2, as well as the reduction of NO oxidation reaction, RO2 + NO → RO + NO2, RO + O2 → HO2 etc. are expected. How the difference in the effect of HR(HO2) and HR(RO2) shown in Figs. 11 and 12 can be explained by these factors?

Author's response: We added an explanation for better clarifying the difference between the role of HO2 and RO2 uptakes. Both HR(HO2) and HRs(RO2) suppress the NO oxidation, which is respectively via reactions (R1) and (R2-R3-R1): HO2 + NO → OH + NO2 (R1) RO2 + NO → RO + NO2 (R2) RO + O2 → R'O + HO2 (R3) Thus, the uptakes of HO2 and RO2 both preserve high NO/NOx ratio and generally restrict OH and O3 formations (Fig. 11 i, j, m, n). However, less RO2 participating in the hydrocarbon oxidation only reduces OH and O3 levels at polluted region while enhances OH level and leave no significant effect on O3 at remote regions (Fig. 12 i, j, m, n), due to the different oxidizing mechanisms for HCs between polluted and remote regions. Moreover, HRs(RO2) do suppress the formations of PAN and other organic nitrates. Less PAN is produced, which means more NOx are preserved, esp. at the lower troposphere. Fig.12 l showed a doubly maximum increase for NOx at the surface (144%) compared to the maximum NOx increase seen in Fig. 11 l (66%), due to

reducing effects by HRs(RO2) for both NO oxidation and PAN formation. We provided the additional explanation for our manuscript at L543-569.

Referee's comment: 2. Other than the well-known heterogenous processed of N2O5, HO2 and RO2 analyzed in this study, the heterogeneous renoxification process of HNO3 to reproduce NOx has previously been suggested in order to explain the model overestimate of HNO3/NOx ratio in the free and polluted atmosphere (Hauglustaine et al., Geophys. Res. Lett., 23, 2609-2612, 1996: Lary et al., J. Geophys. Res., 102, 3671–3682, 1997; Li et al., SOLA, 11, 124–128, 2015; Akimoto et al., Atmos. Chem. Phys., 19, 603-615, 2019). Although the importance of this process has not been established, the same tendency of overestimate of HNO3 and underestimate of NOx has been revealed in this study (Table 5). Discussion should be given for the possibility of the heterogeneous reaction of HNO3 whether in supporting or objecting.

Author's response: We thank for the suggestion from the Referee. In the original text, the comparison with ground observations for EANET and EMEP still showed low correlations for HNO3 (0.177 for EANET, 0.116 for EMEP – Table 5). In Fig. S9, the model correlations with EANET and EMEP observations for HNO3 and NOx showed higher tendencies for HNO3 overestimates and NOx underestimates at low levels of HNO3 (0-1 ppb) and high levels of NOx (>10 ppb), which indicate the highly polluted sites. For remote regions covered by ATom1 flights, our model showed relatively large overestimates for NOx at the surface layer (Fig. 6 a,e). The low reproducibility of model for NOx could be due to the low horizontal resolution of the simulations ($\sim$ 2.8o). Higher resolutions could improve the model reproduction for surface NOx as previously investigated by Sekiya et al. (Geosci. Model Dev., 11, 959–988, 2018).

The heterogeneous "renoxification" reaction of HNO3 on soot surface (R4), which is suggested by the Referee, could also be a possible solution: HNO3 + soot $\rightarrow$ NO + NO2 (R4). The additional (R4) followed by NO2 uptakes onto soot: NO2 + particles $\rightarrow$ 0.5 HONO + 0.5 HNO3 (R5), can be expected to increase NO, and decrease O3 via the consequent titration reaction. These changes could reduce the model overestimates

for HNO3 and O3, and the model underestimates for NOx with EANET and EMEP stations.

A concerning NOx chemistry regarding HONO formation is already considered in another report (preparing for submission), coupling several HONO reactions including (R5). Without (R4)'s inclusion, the whole HONO chemistry could either increase or decrease HNO3 at EMEP and EANET stations during winter and summer conditions, resulting in slight reductions for model bias with EANET and EMEP for HNO3. However, the comparison with ground observations for NOx was not improved. When we incorporate (R4) into the model, the NOx chemistry did not undergo an effective "renoxification" to enhance NOx concentrations over EANET. To be able to conclude whether the "renoxification" process could remedy the issue, further examination would be required.

We revised our manuscript based on the above explanation at L267-276.

Referee's comment: 3. Many of the figures are rather poorly presented for readers and should be revised. (1) In most of the figures, size of inside letters and axis labels are too small (unreadable on print and difficult to read even on PC screen). (2) Fig.3: How the site for each species were selected? There is no explanation in the text. (3) Figs. 3, 4, 5: The difference between the plots for noHR_n2o5, _ho2, _ro2 and _CLD are almost undiscernible. It is suggested to show only noHR and STD in these Figures, and the difference of noHR_n2o5, _ho2, _ro2 and _CLD should be presented in some selected plots in a different Figure. (4) Figs. 9, 11, 12: The differences between the upper and lower figures are not discernible easily. It is suggested to delete the figures for HRS(N2O5-aerosols), HRS(HO2-Cloud) and HRS(RO2-Cloud) in these Figures. It would be enough to explain in the text that the uptake of N2O5 on aerosols, and that of HO2 and RO2 on cloud are major processes. Explanation should be given in the text why the process predominate for each of the species. (5) Figs. 10, 14: Labels and units of horizontal axis should be given properly.

Author's response: (1), (5) We acknowledged the responsibility for the figures' readability. We considerably modify each figure in the revised version upon the Referee's suggestions. (2) We revised Fig. 3 with presenting the median value of grouped stations as Chinese region (stations in China and South Korea), remote stations with low NOx levels of EANET, and all EMEP stations. (3) In Fig. 3,4,5, we separate plots of each HR impacts from the concentration plots, at which we keep only noHR and STD's comparison with measurements. (4) Figures for HRS(N2O5-aerosols), HRS(HO2-Cloud) and HRS(RO2-Cloud) are moved to the Supplement.

Referee's comment: 4. Table 2: What is the meaning of asterisk for "product*". What do the ISO2 and MACRO2 stand for?

Author's response: The asterisk for "product*" in Table 2 was meant to represents a remaining error of expression and was deleted in the revised version. ISO2 denoted for peroxy radicals from C5H8+OH, and MACRO2 stands for peroxy radicals from the oxidation of MACR, methacrolein (CH2=C(CH3)CHO). These descriptions were provided in the revised version at L194-195.

Referee's comment: 5. Tables 5, 6, 7, 8: Units should be given appropriately.

Author's response: We provided the units in these tables appropriately in the revised version.

Sincerely,

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

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