Comments by referees are in blue.
Our replies are in black.
Changes to the manuscript are highlighted in red both here and in the revised manuscript.

Reply to referee #1

This paper investigated the heterogeneous N_2O_5 uptake and $ClNO_2$ production on the saline mineral dust through laboratory experiments, and evaluated the impacts of this heterogeneous process on tropospheric $ClNO_2$ using a 3-D model. The results showed substantial formation of $ClNO_2$ from the heterogeneous process on different saline mineral dust samples, and the $ClNO_2$ yield varied with the mass fraction of particulate chloride and RH. The model simulation also showed significant impacts of this heterogeneous process on $ClNO_2$ production and even O_3 formation during a severe dust event in China. This study provides valuable information on the heterogeneous process of N_2O_5 and $ClNO_2$ on saline mineral dust particles, the information of which has been very limited. The results will be useful to better understand the impacts of this heterogeneous process in different environments, and also will be helpful to improve the air quality model performance. Overall, the manuscript is well written, and thus I suggest that the manuscript can be published after addressing the following comments.

Reply: We would like to thank ref#1 for reviewing our manuscript and recommending it for publication after minor revision. We have carefully addressed all the comments and revised our manuscript accordingly, as detailed below.

Line 152-153, please clarify what does the 'initial N_2O_5 concentrations' mean. Does the author mean the N_2O_5 generated from the reaction chamber or before passing the sample filters?

Reply: It is a good point. In response to this comment, we have deleted the sentence (in Section 2.2.1) describing initial N_2O_5 concentrations, and provided this information in Section 2.2.2 (page 9) we have revised this sentence for better clarity: "As shown in Figure 1, the mixed flow (2610 mL/min) could be directed through a blank PTFE membrane filter (47 mm, Whatman, USA) housed in a PFA filter holder, and in this case initial N_2O_5 and $ClNO_2$ concentrations were measured; in our experiments, initial N_2O_5 concentrations were in the range of 0.4-1.0 ppbv." After revision, it is clear that initial N_2O_5 concentrations are those in the mixed flow immediately before it is passed through the sample filter.

Line 162, although the dust particle loading method has been introduced in previous studies, a brief description will be useful and should be included here.

Reply: In the revised manuscript (page 9) we have added one sentence to further describe how we prepared our filter samples: "Saline mineral dust particles were loaded onto PTFE filters using the method described in our previous study (Li et al., 2020; Jia et al., 2021). In brief, 10 mL particle/ethanol mixture was transferred onto a PTFE filter, and after ethanol was evaporated a relatively uniform particle film, as revealed by visual inspection, was formed on the filter."

Line 193-196 and Line 373-375. In addition to the uptake and yield on dust particles, the parameters used for non-dust particles also should be explicit. Some information needs to be briefly provided in the main text or supplementary.

Reply: As suggested, we have made the following change in the revised manuscript (page 11): "…is used in this study, and more details can be found in the supplement." We have also updated the supplement accordingly to describe the parameterization we used.

Line 201, the detection limit for these species should be provided in the experimental section.

Reply: Detection limits can be found in the Appendix. As suggested by the referee, in the revised manuscript we have moved such information to Section 2.2 (page 10): "The detection

limits were 2 pptv for N_2O_5 and 3 pptv for $ClNO_2$, calculated as four times of standard deviations (4 σ) when measuring blank samples with 1 min average, and the accuracy was estimated to be ~25%."

Table 2. Considering the errors given by the standard deviation, the author should avoid using excessive significant digits. This also needs to be checked thoroughly for the whole manuscript.

Reply: We have thought carefully about this comment. The referee is absolutely right, and it may be more proper to use 0.01 for the significant digits. However, as shown in Table 2, $ClNO_2$ yields are <0.01 in some cases, and therefore we would like to use 0.001 for the significant digits.

Figure 3. Please clarify the meaning of particulate water, and definition of m_w/m_0.

Reply: In the revised manuscript (page 14) we have modified the caption of Figure 3 to clarify the meaning of particulate water and define m_w/m_0: "Measured $ClNO_2$ yields (black symbol) and m_w/m_0 (red line) as a function of RH for (a) H1 and (b) H2. The error bar represents standard deviation, and m_w/m_0 represents normalized mass of particulate water (normalized to the mass of dry particles), which was measured as the relative increase in particle mass at a given RH compared to <1% RH." In addition, we have also modified the captions for Figure 4 (page 15) and 5 (page 16) accordingly.

Line 285-290. It's interesting to see that the Ca and Mg amount may affect the $ClNO_2$ yield. Can any figures or plots better depict the dependence of $ClNO_2$ yields on Ca and Mg concentration or fraction in the saline mineral dust samples?

Reply: As suggested, to better illustrate the effects of Ca^{2+}, in the revised manuscript (page 17) we have made the following modification: "…and as shown in Figure S1, the amounts of water soluble Ca^{2+} in the four samples (H1, H2, M1 and M3) with larger $\varphi(ClNO_2)$ at 18% RH were significantly larger than those in the other four samples (M2, M4, L1 and L2)." In addition, a new figure (Figure S1) has been added into the SI accordingly.

Mg^{2+} may not play an important role in $ClNO_2$ production lower RH, as in our saline mineral dust samples Mg^{2+} usually appears together with SO_4^{2-} (instead of Cl^-).

Line 331-332, as the author stated later, the assumption that all chloride is soluble may lead to overestimated $ClNO_2$ yield. What would be a more reasonable assumption here, any semi-quantitative information on the water-soluble Cl fraction/content can be inferred? Is there previous data that can be used to compare the $[Cl]/[H_2O]$ ratio on the dust samples with the normal ambient particles? I think this will be very useful for further modeling simulation works.

Reply: This is a good point. As $[Cl^-]$ in aqueous solutions change dynamically with RH, currently we cannot directly measured $[Cl^-]/[H_2O]$. We can use aerosol thermodynamic models to calculate $[Cl^-]/[H_2O]$; however, our previous work (Zhang et al., 2019) found that ISORROPIA-II failed to predict aerosol liquid water contents for some of the saline mineral dust samples.

On the other hand, at 75% RH most of (if not all) chloride should be dissolved into aqueous phase, as significant water uptake was observed at 75% RH. In the revised manuscript (page 20) we have added one sentence to discuss this issue: "First, even at ~75% RH (the highest RH at which our experiments were conducted), chloride contained in saline mineral dust may not be fully dissolved, and therefore our calculation may overestimate $[Cl^-]/[H_2O(aq)]$ and thus also overestimate $\varphi(ClNO_2)$. This effect should not be large as significant water uptake was observed at ~75% RH for saline mineral dust sample we examined (Figures 3-5)."

Line 365, can the author explain more the rationale for choosing 0.1 as the fixed ClNO2 yield in the model simulation?

Reply: In the revised manuscript (page 21) we have made the following change to further explain the rationale for choosing 0.1 as the $ClNO_2$ yield and to further explain the purpose of our

modeling work: "This value, which is at the low end of our measured range of $\varphi(ClNO_2)$ (<0.05 to ~0.77), is higher than those determined in our work for low chloride samples but lower than those for medium chloride samples. The purpose of our modeling work, is to preliminarily assess whether N_2O_5 uptake onto saline dust as a potential source of $ClNO_2$ may have important effects on tropospheric chemistry."

Line 397-399. The 'short' night in summer may still be enough to accumulate $ClNO_2$ with plenty of NOx, O_3, and particles. The statements here need further revision and improvement.

Reply: This referee is right. What we actually want to express is that $ClNO_2$ may be more important in winter and spring (due to longer nights) than summer (due to shorter nights). In the revised manuscript (page 24) we have modified the sentence to make our statement more proper: "…and is conducted in summer when $ClNO_2$ is more difficult to be accumulated due to short night (compared to winter and spring with long nights)."