Response to Comments

Reviewer #2:

Tan et al. report the measurements of $ClNO_2$, NO_2, O_3 and related parameters for three seasons in 2019, obtained during the Jülich Atmospheric Chemistry Project (JULIAC) campaign in Germany. An important result of this study is the variations of $ClNO_2$ production efficiency in different seasons, which are most sensitive to the availability of NO_2 and increase with the decreasing temperature. This finding is valuable as it enhances our understanding on the dependence of $ClNO_2$ formation on the availability of NO_2 and O_3 in Europe. Overall, the manuscript is well presented, however, I feel that the importance of the study and discussion of results can be further strengthen and improved. My comments are as below.

We thank the reviewer for the useful comments/suggestions. Please, find below our answers and the related revisions (in blue) to the manuscript

1. *Line 19: Delete the word 'ion' (same for line 52)*

   Answer: Done.

2. *Line 22: Please specify the date instead of using 'one night in September'*

   Answer: We specify it as "…in the night of September 20."

3. Line 58: The yield for $ClNO_2$ (φ_{ClNO_2}) can be equal to 0 or 1, therefore, it should be ≤

   Answer: Corrected

4. *Line 62–63: 'The forward and back reactions constitute a fast thermal equilibrium between NO_3 and N_2O_5 that is established within a minute at room temperature.' Revise this sentence by justifying how the equilibrium can be establish within a minute. Is this base on the authors' calculation or from the literature? The concentration of NO_2 can also influence the equilibrium of NO_3 and N_2O_5*

Answer: We revised the sentence as “The forward and back reactions constitute a fast thermal equilibrium between NO_3 and N_2O_5 that is quickly established at temperatures typically found in the lower troposphere (Brown and Stutz, 2012).”

5. *Line 75: $ClNO_2$ usually present at night but not always is the case. Suggest to delete the word ‘only’*

   Answer: The word “only” here refers to N_2O_5 not to $ClNO_2$. We revised the sentence as “Therefore, significant concentrations of N_2O_5 (the precursor of $ClNO_2$) are usually only present at night.”

6. *Line 123: The authors should highlight in the introduction or conclusion why investigation on the seasonal variation of $ClNO_2$ concentrations and its formation are scientifically important*

   Answer: We revised the last paragraph of the introduction as “In this work, the seasonal variation of $ClNO_2$ concentrations and its formation are investigated. As mentioned above, previous studies have demonstrated that $ClNO_2$ concentrations show significant seasonal variations (Mielke et al., 2016;Sommariva et al., 2018). However, intensive seasonal measurements in central Europe, to our knowledge, have not been performed so far. Given the ubiquitous nature of $ClNO_2$ and its importance to enhance atmospheric oxidation processes, more detailed studies are needed to broaden our knowledge of atmospheric $ClNO_2$ levels, its seasonal behavior and its distribution in environments with different chemical conditions. In addition, this work presents empirical production efficiencies of $ClNO_2$ determined from the nighttime measurements of $ClNO_2$, NO_2 and O_3 and analyzed for their seasonal variations and origin of air masses, a prerequisite to understand the contribution of $ClNO_2$ to radical photochemistry under the chemical and meteorological conditions encountered in this campaign. Finally, a chemical box model is used here to understand the dependence of $ClNO_2$ formation and production efficiency on the observed nocturnal O_3 and NO_2 concentrations. The measurements and analysis presented in this paper help to illustrate the seasonal variability of $ClNO_2$ concentrations and shed light on the factors that control its production in different seasons.”

7. *Line 168: The concentration of Cl_2 in the cylinder used for calibration is 5 ppmv (±5%). As we know Cl_2 is a very reactive gas that can loss on surfaces. Is this ± 5% a reliable value? The authors should provide details on whether they have quantified the output concentration of Cl_2 from the cylinder and/or consider the potential loss of Cl_2 in the calibration system, e.g. the loss on the regulator of the cylinder or tubing? This is crucial for the determination of $ClNO_2$ calibration factor*

and estimation of measurement uncertainty, which can affect the reported levels of $ClNO_2$ and maybe the conclusions of this study.

Answer: As explained from Line 169 to 173, the $ClNO_2$ concentration in the calibration air is determined by measuring the NO_2 concentration after thermally decomposing $ClNO_2$ to Cl and NO_2. Thus, the absolute concentration of Cl_2 does not influence the production of $ClNO_2$ or the accuracy of the calibration. As long as there is enough and stable Cl_2 supply to the calibration unit, certain amount of ClNO2 is produced. The presence of Cl_2 is confirmed by the CIMS. The sentence about the uncertainty of Cl_2 is misleading, and we deleted the sentence.

8. *Line 279: Specify the humidity (RH) of the humidified chamber air*

   Answer: Done.

9. *Line 300: 'no corrections are needed for the interpretation of $ClNO_2$ measurements'. I am wondering if this variation has been considered in the estimation of the measurement uncertainty.*

   Answer: It was not considered in the measurement uncertainty given its low influence on the measurement (<1%).

10. *Line 367: As shown in this figure, the $ClNO_2$ and related parameters are separated into long-range transport and region transport. The classification of long-range and regional has been described in the text. A lacking information here is the 'age' of different air masses. My question is will the 'age' of air masses play important role in the observed levels of $ClNO_2$? I think this should also be addressed in the discussion since the 'age' of air mass may affect the NO_2 and O_3 concentrations*

    Answer: We have added the following sentence to address the potential difference of 'age' between the two cases: "The age of the airmass could play a role in the observed levels of $ClNO_2$ due to the impact on NO_2 and O_3 concentrations, and hence on $ClNO_2$. As shown in Fig. 2, regionally transported air masses spend more time over urban areas picking up anthropogenic emissions (indicated by high NO_2 mixing ratios). They also have more time for the photochemical processing of pollutants compared to the long-range transported air masses. In the cold months (February, November, and December), long reaction times would lead to lower O_3 concentrations for the regional air masses

due to the titration by anthropogenically emitted NO compared to conditions in August and September when photochemical ozone production is more efficient than the titration effect."

11. *Line 387: Section 3.3 describes the nocturnal vertical stratification and summarize that the JULIAC inlet (50 m) is most often located within the nocturnal boundary layer and on top of the surface layer. What does it mean by most often? At this point, I am not so convinced yet that the $ClNO_2$ are often measured above the nocturnal boundary layer with the discussion and provide only one day example (Fig.4). Please provide more evidence (of different seasons) and discussion in the main text or supporting info to support this argument. This is an important information for the validity of the calculation made from Eq7 (Line 465)*

Answer: As NO can be regarded as an indicator of surface interruption, we added a plot Fig. S8 to show the cumulative frequency of measured NO concentrations to indicate the influence from surface interaction. We also added discussion at the end of section 3.3 "…when air was temporarily impacted by surface interaction only constitute a small fraction of the measurement time. To quantify the influence of surface interactions, elevated NO concentrations at the sampling point can be used. For more than 90% of the time, measured NO mixing ratios are lower than 0.1 ppbv (Fig. S8, Supporting Information) indicating that air masses were typically little influenced by surface emissions. Therefore, it can be assumed that the sampling point was most often located in the nocturnal boundary layer. Median values further analyzed in this work are therefore representative of conditions in the nocturnal boundary layer."

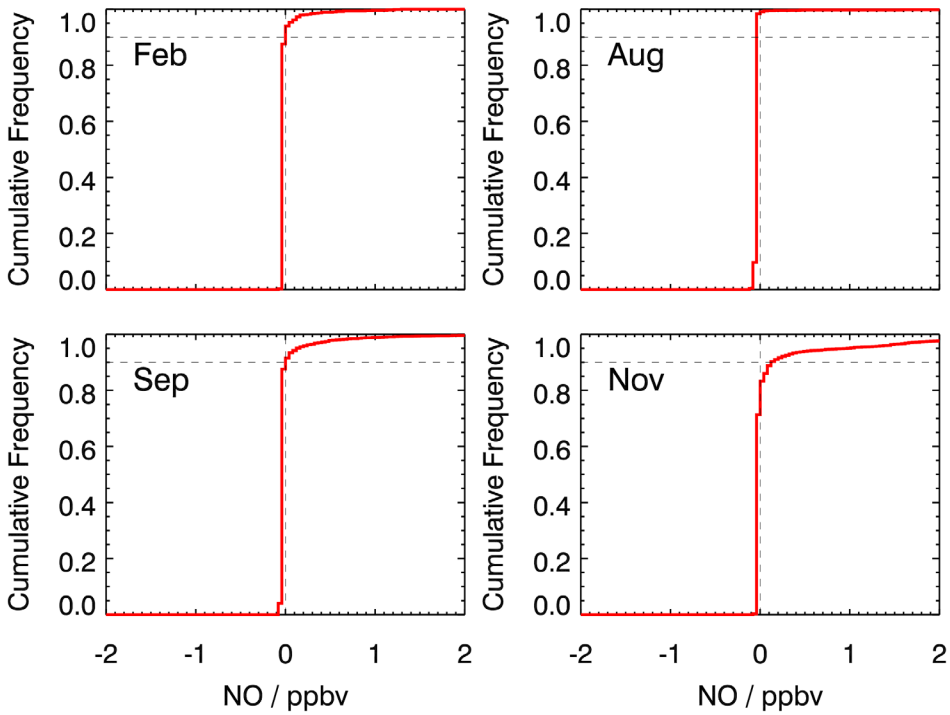

Figure S8. Cumulative histogram of measured NO concentrations during nighttime for different periods. The horizontal lines denote the position of 90% percentile of data.

12. *Line 541–542: The measured aerosol surface area is an essential parameter for the calculation. This should be included in the supporting info. Can the authors justify why setting the aerosol surface area to constant value in the model since they have measurement data?*

    Answer: We agree that the aerosol surface area is an important parameter to calculation the $ClNO_2$ production. However, the measurement was only conducted inside the chamber, which could be significantly changed by the sampling system (blower). We included the measured aerosol surface area data in Table S1 in the Supplement to show the order of magnitude of this parameter and added the following sentence at line 591 to address this issue "In this model calculation, the aerosol surface area S_a is held constant instead of using the *value* measured inside the chamber, which was likely impacted by the sampling system but cannot be corrected for ambient measurement (Section 2.3). Nevertheless, the measured S_a gives some confidence that the model is not using an unrealistic lower limit."

13. *Line 577–578: Temperature also plays an important role for the value of the $ClNO_2$ production efficiency due to the shift of the equilibrium between NO_3 to N_2O_5. The temperature shift may also affect the humidity which has been shown*

in previous studies to promote N_2O_5 uptake and production of $ClNO_2$. How can the authors separate the effect of humidity with the effect of temperature?

Answer: In the simplified model, it's difficult to separate the effect between temperature and humidity. Instead, the ambient water content concentration is held constant, which means the RH increase with higher temperature in the model (Fig 6 (b) and (d)). As the yield of $ClNO_2$ and N_2O_5 uptake coefficient are held constant, the modelled $ClNO_2$ concentrations are not sensitive the change of RH.

14. *Line 691: Please provide a proper reference here rather than citing the general website of IUPAC*

    Answer: Done.

15. *Supporting Information Figure S2: Explain why the response of $ClNO_2$ decrease with H_2O concentration (a)? Show the correlation coefficient for this linear fitting (b) as the points are spreading wide from the fitted-line.*

    Answer: We added the linear correlation coefficient (R^2) to Figure S2. We also added a sentence in the caption to explain the decreasing trend of $ClNO_2$ signal "The decreasing trend of the $ClNO_2$ signal with increasing humidity reflects the fact that the reaction of $ClNO_2$ with higher-order clusters of $I^-\cdot(H_2O)_n$ is slower than that with $I^-\cdot(H_2O)$ alone (Kercher et al., 2009;Slusher et al., 2004)."

References

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