## **Response to Comments**

## Reviewer #1:

This manuscript presents observations of nitryl chloride (CINO<sub>2</sub>), along with several precursor compounds, measured over several seasons at 50m above the surface at a rural site in western central Europe. CINO<sub>2</sub> is an important source of the powerful atmospheric oxidant atomic chlorine and has been shown to demonstrate significant spatial variability due to its relatively complex production mechanism. Although many measurements have been made of CINO<sub>2</sub> at surface locations, the reduced concentrations close to nitric oxide (NO) emissions mean it is likely to be more efficiently produced in the nocturnal residual layer, from where subsequent mixing will allow it to influence surface photochemistry on the following day. The observations presented here are predominantly from within the nocturnal residual layer, and thus represent a significant contribution to the growing body of data on mid-continental CINO<sub>2</sub>.

The authors present the  $CINO_2$  data, and use co-located measurements of  $CINO_2$ precursors to calculate a CINO<sub>2</sub> production efficiency to compare across the measurement period. This is a useful parameter on which to focus, as the complex nature of CINO2 production results in significant variability, making it often difficult to constrain in models. The authors then use a chemical box-model to explore the effects of ozone  $(O_3)$ , nitrogen dioxide  $(NO_2)$  and temperature on CINO<sub>2</sub> production across the experienced parameter space. This analysis is insightful; however, I feel the authors need to do more to demonstrate the sensitivity of their analysis and conclusions to other important parameters that control CINO<sub>2</sub> production. In particular, the sensitivity to the loss rate of the nitrate radical (NO<sub>3</sub>) to reaction with volatile organic compounds (VOC) warrants a more detailed sensitivity analysis than that presented in Fig. S9. The correlation between measured particulate chloride and calculated CINO<sub>2</sub> production efficiency should also be shown to support the argument made that this is not a limiting factor. Overall, the manuscript is well written and represents a valuable contribution to the field, and warrants publication in ACP once the following comments have been addressed.

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

 As particle surface area and chloride content are key factors in the production of CINO<sub>2</sub>, it would be useful for the reader if these data were presented somewhere in the paper or supplement and discussed in more detail. In section 3.4 the authors argue that CINO<sub>2</sub> production efficiency is not limited by particle chloride content, but I feel this statement would be better supported if the particle data were shown. Multiple factors can influence both the uptake of  $N_2O_5$  to particles and the subsequent yield of CINO<sub>2</sub>, such as chloride molarity and liquid water content. The authors acknowledge that they do not have sufficient data to fully characterize the particle phase, however, more could be done to demonstrate the sensitivity of the system to these parameters (e.g., McDuffie et al. 2018).

**Answer**: We agree that the aerosol surface area, the liquid water content and chloride concentration are important parameters to determine the CINO<sub>2</sub> production. However, aerosol measurements were only conducted inside the chamber, and could be significantly affected by the sampling system (blower) and by the large surface of the chamber. We included the measured aerosol surface area data and calculated the liquid water content using aerosol thermal dynamic model ISORROPIA2 in Table S1 in the Supplement. The aerosol chemical composition is shown in Table S2. We modified the discussion starting 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.

The aerosol chemical composition also plays a role in determining the production efficiency. The yield of CINO<sub>2</sub> from N<sub>2</sub>O<sub>5</sub> heterogenous reaction ( $\phi$ (ClNO<sub>2</sub>)) can be expressed by assuming that the production of CINO<sub>2</sub> results from the competition between Cl<sup>-</sup> and H<sub>2</sub>O reacting with the H<sub>2</sub>ONO<sub>2</sub><sup>+</sup> intermediate formed from the N<sub>2</sub>O<sub>5</sub> uptake on aerosol (Bertram and Thornton, 2009;Mielke et al., 2013;McDuffie et al., 2018).

$$\varphi(\text{CINO}_2)_{\text{par}} = \left(1 + \frac{[\text{H}_2\text{O}]}{50[\text{Cl}^-]}\right)^{-1}$$
 (Eq. 8)

The value of the CINO<sub>2</sub> yield is different in the periods of the campaign showing maximum values of 0.6 to 0.8 in February (Fig. S14). This is consistent with the relatively high CINO<sub>2</sub> production efficiency derived from the integrated production rate of NO<sub>3</sub> (Eq.7). However, the calculated CINO<sub>2</sub> yield decreases below 0.4 in August and September, which could be attributed to the higher aerosol liquid water content in these two periods compared to the value in other periods (Table S1). The calculated CINO<sub>2</sub> yield is also higher for the long-range transported air masses than those for the regional one (Fig. S14, Supporting Information). The relatively high CINO<sub>2</sub> production efficiencies found in the regional air masses, which are in contrast to their relatively low calculated  $\phi(CINO_2)$ , suggest that other factors play an important role in determining the CINO<sub>2</sub> production such as larger-than-assumed uptake coefficient for N<sub>2</sub>O<sub>5</sub> and/or aerosol surface area."

We also added the calculated  $\varphi(CINO_2)$  in the supplement.



**Figure S14.** Scatter plot of calculated CINO<sub>2</sub> yield ( $\varphi$ (CINO<sub>2</sub>)) versus the ratio between chloride and aerosol liquid water content. Parameterized values of  $\varphi$ (CINO<sub>2</sub>) are calculated following literatures recommendations (Bertram and Thornton, 2009;Mielke et al., 2013;McDuffie et al., 2018). Red and blue dots denote the average for the regional and long-range transported air masses, respectively. In September, the data for long-range transported air masses case is missing due to the lack of simultaneous aerosol chemical composition measurements.

2. As with comment 1, the conclusions of the work would be better supported if the sensitivity to the gas phase loss of NO<sub>3</sub> to VOC reaction was demonstrated (beyond that shown in Fig. S9). In the modelling work presented in Sect. 3.5 the authors assume a constant NO<sub>3</sub> reactive loss rate (k<sub>NO3</sub>) of 0.001 s-1. As this work is carried out across both summer and winter seasons, and due to the strong biogenic control of the k<sub>NO3</sub>, it seems unlikely that this constraint is valid. Observations of k<sub>NO3</sub> at another site in Germany have shown k<sub>NO3</sub> values approaching 0.3 s<sup>-1</sup> (Liebmann et al. 2018). Although the authors do carry out a set of simulations with a value of k<sub>NO3</sub> = 0.0005 s-1, a more thorough assessment of the model sensitivity to this parameter would better support the authors assumption that it plays a minor controlling role.

**Answer:** We acknowledge that the NO<sub>3</sub> reactivity is one of the major uncertainties in our model calculation. As discussed in the response of comment 3, the NO<sub>3</sub> reactivity used in the model has been increased to match the

observed CINO<sub>2</sub>. The comparison to the observation serves as a justification of the choice of  $k_{NO3}$ . Liebmann et al. (page 12049-12050) report "Campaign-averaged values were low (~0.01 s-1) during night-time but a factor of 10 larger ~ 0.1 s-1 at 14:00UTC (local 16:00)." They state "The elevated location of the Hohenpeissenberg observatory, located on a mountain top above the surrounding countryside, favored sampling from the residual layer and free troposphere at night-time. In the absence of turbulent exchange, the residual layer and free troposphere may become disconnected from the planetary boundary layer (PBL) and thus from ground-level emissions of reactive trace gases; the layers may thus contain low levels of biogenic trace gases as well as low(er) levels of NO<sub>2</sub> and higher levels of ozone." In our paper we also argue that we measured most of the time in the NBL that was disconnected from ground emissions. Therefore, we used their reported nighttime values of 0.01 s<sup>-1</sup> as a reference for comparison with JULIAC, as we assume that CINO2 is formed mainly at night.

We added a sentence in Line 538 "The assumed value of the NO<sub>3</sub> loss rate,  $k_{NO3}$ , is adjusted, so that the modelled CINO<sub>2</sub> concentration agrees with the magnitude of the observations (Fig. S10, Supporting Information), which corresponds to an NO<sub>3</sub> reactivity of 0.004 s<sup>-1</sup>." We also added in Line 591 "Though the purpose of this model calculation is not to reproduce the observations, it is critical to address the related uncertainties/limitations due to the assumptions in the simplified model. The key parameters affecting the formation of CINO<sub>2</sub> concentrations are temperature, NO<sub>3</sub> loss, N<sub>2</sub>O<sub>5</sub> loss. Their impact on the model results<del>ions</del> is discussed below.

•••

As mentioned above, the NO<sub>3</sub> reactivity is assumed to be 0.004 s<sup>-1</sup> to match the observations, which is comparable to the NO<sub>3</sub> reactivity observed at a mountainous site in south Germany with a campaign-averaged value of 0.01 s<sup>-1</sup> for nighttime conditions (Liebmann et al., 2018). As shown in the sensitivity test, a higher NO<sub>3</sub> reactivity leads to lower modelled CINO<sub>2</sub> concentrations. Therefore, the low NO<sub>3</sub> reactivity in the model could be regarded as a lower limit given the similar biogenic-influenced environments."

3. It would be useful if the observations overlaid on the model isopleths in Fig. 6 (a) and (b) showed the observed CINO<sub>2</sub> mixing ratios to compare with the model values. Although the purpose of the modelling is not to recreate the observations, rather to investigate the chemical sensitivities of the system, it would provide confidence in the model's ability to accurately represent the chemistry if the general observational trends were recreated.

**Answer:** We have to admit that it is very difficult to add the CINO<sub>2</sub> observation data in the isopleths in Fig. 6. Instead, we extract the modelled results from the isopleth plots, which are compared with the observation data and added a new figure to the Supplement (Fig. S10). We agree that the comparison helps to provide confidence on the model's ability to represent the chemical conditions. In fact, with the help of this comparison, we realize that the original model used too small  $k_{NO3}$  and overpredicted the modelled CINO<sub>2</sub> concentrations. In the revised manuscript, the  $k_{NO3}$  is increased from 0.001 to 0.004 to better reproduce the magnitude of CINO<sub>2</sub> (see answer to previous question).

We added a sentence in Line 562 "Following Sommariva et al. (2018), a constant NO<sub>3</sub> loss rate is used to represent the typical loss of NO<sub>3</sub> radicals ( $k_{NO3}$ ) in their reactions with organic compounds (Reaction R5). The assumed value of the NO<sub>3</sub> loss rate  $k_{NO3}$  is adjusted so that the modelled ClNO<sub>2</sub> concentration agrees with the magnitude of the observations (Fig. S10, Supporting Information), which corresponds to an NO<sub>3</sub> reactivity of 0.004 s<sup>-1</sup>."



**Figure S10.** Comparison between observed and modelled  $CINO_2$  for the regional (left) and long-range (right) transportation air masses. Model results are calculated as done in Fig. 6 in main text but measured  $O_3$  concentrations and temperature data are used as input.

## References

- Bertram, T. H., and Thornton, J. A.: Toward a general parameterization of N2O5 reactivity on aqueous particles: the competing effects of particle liquid water, nitrate and chloride, Atmos. Chem. Phys., 9, 8351-8363, 10.5194/acp-9-8351-2009, 2009.
- Liebmann, J. M., Muller, J. B. A., Kubistin, D., Claude, A., Holla, R., Plass-Dülmer, C., Lelieveld, J., and Crowley, J. N.: Direct measurements of NO3 reactivity in and above the boundary layer of a mountaintop site: identification of reactive trace gases and comparison with OH reactivity, Atmos. Chem. Phys., 18, 12045-12059, 10.5194/acp-18-12045-2018, 2018.
- McDuffie, E. E., Fibiger, D. L., Dubé, W. P., Lopez Hilfiker, F., Lee, B. H., Jaeglé, L., Guo, H., Weber, R. J., Reeves, J. M., Weinheimer, A. J., Schroder, J. C., Campuzano-Jost, P., Jimenez, J. L., Dibb, J. E., Veres, P., Ebben, C., Sparks, T. L., Wooldridge, P. J., Cohen, R. C., Campos, T., Hall, S. R., Ullmann, K., Roberts, J. M., Thornton, J. A., and Brown, S. S.: CINO2 Yields From Aircraft Measurements During the 2015 WINTER Campaign and Critical Evaluation of the Current Parameterization, J. Geophys. Res., 123, 12,994-913,015, 10.1029/2018jd029358, 2018.
- Mielke, L. H., Stutz, J., Tsai, C., Hurlock, S. C., Roberts, J. M., Veres, P. R., Froyd, K. D., Hayes, P. L., Cubison, M. J., Jimenez, J. L., Washenfelder, R. A., Young, C. J., Gilman, J. B., de Gouw, J. A., Flynn, J. H., Grossberg, N., Lefer, B. L., Liu, J., Weber, R. J., and Osthoff, H. D.: Heterogeneous formation of nitryl chloride and its role as a nocturnal NOx reservoir species during CalNex-LA 2010, J. Geophys. Res., 118, 10,638-610,652, 10.1002/jgrd.50783, 2013.
- Sommariva, R., Hollis, L. D. J., Sherwen, T., Baker, A. R., Ball, S. M., Bandy, B. J., Bell, T. G., Chowdhury, M. N., Cordell, R. L., Evans, M. J., Lee, J. D., Reed, C., Reeves, C. E., Roberts, J. M., Yang, M., and Monks, P. S.: Seasonal and geographical variability of nitryl chloride and its precursors in Northern Europe, Atmos. Sci. Lett., 19, e844, 10.1002/asl.844, 2018.