Responses to Editors and Reviewers

We sincerely appreciate the reviewers for their constructive and insightful comments, which are of great benefit to improve the quality of the manuscript. In response, we have carefully revised the manuscript and addressed each comment in a point-by-point manner. For clarity, the reviewers' comments are presented in black, our responses in blue, and the added or revised sections of the manuscript are highlighted in red.

RC1: **'Comment on egusphere-2024-1638', Anonymous Referee #1, 31 Jul 2024**

General Comments

The work by Gaojie Chen et al. is a well written study presenting two months of ambient observations in Southeast China and has two main components. First, the work introduces interesting evidence for the formation of $ClNO_2$ during the daytime by a recently suggested particulate nitrate mechanism. Second, the work discusses the implications for Cl radical production from $ClNO_2$ photolysis.

The first component has significant implications for the understanding of $ClNO_2$ formation globally. However, a discussion of the traditional metrics of $ClNO_2$ formation, the N_2O_5 uptake rate and $ClNO_2$ yield, are completely absent from the paper. Without a discussion on this topic, the authors' conclusion that "NO_3^- photolysis contributed to daytime generation" is severely weakened. In fact, it is based only a machine learning output which gauges the "importance" of NO_3^- influence on $ClNO_2$ as well as a linear regression of $ClNO_2$ with NO_3^- $\times jNO_2 \times$aerosol S_a. In this joint correlation, insufficient evidence is provided to suggest that the photolysis component improves the correlation. As such, I request major revisions in which the authors justify their conclusion by demonstrating that the daytime observations of $ClNO_2$ cannot be explained by traditional N_2O_5 and $ClNO_2$ chemistry.

The second component is based on box modeling from the master chemical mechanism. Aside from a lack of detail on the parametrization used for N_2O_5 uptake and $ClNO_2$ yield, the results presented are generally sound and informative. I request

that the authors include their choice of parametrization in the main text.

Response: Thanks for your valuable comments. Your review comments and suggestions are benefit to improve the quality and readability of this manuscript. We have revised the manuscript appropriately and addressed the reviewer's comments point-by-point for consideration as below.

The first component: We have added the discussions on the N_2O_5 uptake coefficient ($\gamma(N_2O_5)$) and $ClNO_2$ yield ($\phi(ClNO_2)$). Furthermore, we also provided the evidence showing that the daytime observations of $ClNO_2$ cannot be explained by traditional N_2O_5 and $ClNO_2$ chemistry. Please refer to our response to Specific Comment 4 for more details.

The second component: In this study, the box model is employed to evaluate the photochemical effects of $ClNO_2$. The levels of $ClNO_2$ in the box model were constrained by the observed levels of $ClNO_2$ from our field measurements. This approach eliminates the necessity for parameterization of N_2O_5 uptake and $ClNO_2$ yield to determine $ClNO_2$ levels. Therefore, the parametrization for N_2O_5 uptake and $ClNO_2$ yield was not utilized in the box model.

Specific Comments

1. Section 2: A description on the handling of N_2O_5 uptake and $ClNO_2$ yield is absent from the methods. A list of previous papers is provided but it is not clear how these two parameters are handled. Both N_2O_5 uptake and $ClNO_2$ yield will vary with the parameters investigated here (T, RH, etc.). See McDuffie et al.

McDuffie, E. E., Fibiger, D. L., Dubé, W. P., Lopez Hilfiker, F., Lee, B. H., Jaeglé, L., et al. (2018a). $ClNO_2$ yields from aircraft measurements during the 2015 WINTER campaign and critical evaluation of the current parameterization. Journal of Geophysical Research: Atmospheres, 123(22), 12994–13015. https://doi.org/10.1029/2018JD029358

McDuffie, E. E., Fibiger, D. L., Dubé, W. P., Lopez-Hilfiker, F., Lee, B. H., Thornton, J. A., et al. (2018b). Heterogeneous N_2O_5 uptake during winter: Aircraft measurements during the 2015 WINTER campaign and critical evaluation of current

parameterizations. Journal of Geophysical Research: Atmospheres, 123(8), 4345–4372. https://doi.org/10.1002/2018JD028336

Response: Thanks for your comment. In this study, the box model is employed to evaluate the photochemical effects of $ClNO_2$. The levels of $ClNO_2$ in the box model were constrained by observed levels of $ClNO_2$ from our field measurements. This approach negates the need for parameterization of N_2O_5 uptake and $ClNO_2$ yield to determine $ClNO_2$ levels. Therefore, the parametrization for N_2O_5 uptake and $ClNO_2$ yield was not utilized in the box model. In the section of analyzing $ClNO_2$ production and loss processes, we have added the discussions on the N_2O_5 uptake coefficient ($\gamma(N_2O_5)$) and $ClNO_2$ yield ($\phi(ClNO_2)$). Please refer to our response to Specific Comment 4 for more details.

Added/rewritten: "Due to the levels of $ClNO_2$ in the box model determined by observed levels of $ClNO_2$, the parametrization for N_2O_5 uptake and $ClNO_2$ yield was not utilized in the box model."

"The N_2O_5 uptake coefficient ($\gamma(N_2O_5)$) and $ClNO_2$ yield ($\phi(ClNO_2)$) were estimated using the observational data and parameterization. We derived the values of and $\phi(ClNO_2)$ based on increased rates of $ClNO_2$ and particle nitrate (NO_3^-) in the field observation (Phillips et al., 2016). Specially, $\gamma(N_2O_5)$ and $\phi(ClNO_2)$ were calculated by Eq. (S5) and (S6).

$$\gamma(N_2O_5) = \frac{2 \times \left(P(ClNO_2) + P(NO_3^-)\right)}{cN_2O_5 S_a [N_2O_5]} \quad (S5)$$

$$\phi(ClNO_2) = 2 \times \left(1 + \frac{P(NO_3^-)}{P(ClNO_2)}\right)^{-1} \quad (S6)$$

Here, $P(ClNO_2)$ and $P(NO_3^-)$ represent the production rates of $ClNO_2$ and NO_3^- induced by N_2O_5 uptake, respectively. S_a denotes the aerosol surface area, and $c(N_2O_5)$ is the mean molecular speed of N_2O_5. This method assumes that air masses remain relatively stable, and $ClNO_2$ and NO_3^- were produced through nighttime N_2O_5 heterogeneous uptake. More details on the method are provided elsewhere (Tham et al., 2018; Niu et al., 2022; Phillips et al., 2016). Using the method and selection criteria, we derived $\gamma(N_2O_5)$ and $\phi(ClNO_2)$ during the whole measurement period."

2. Section 3.1: There is no uncertainty presented with the observations in the main text. Please include the uncertainties as the uncertainties in the SI are non-negligible (~20 %).

Response: Thanks for your comment. We have included the uncertainties in the main text.

Added/rewritten: "The uncertainties of the $ClNO_2$ and N_2O_5 measurements were estimated to be ~20 %."

3. Figure 5: What is the interpretation of negative "importance factors"? During the daytime, N_2O_5 is a negative importance factor. Please discuss this in the main text.

Response: Thanks for your comment. In the XGBoost-SHAP model, SHAP values are used to quantify the contribution of each feature to the prediction values, with a negative SHAP value indicating a negative contribution. Generally, negative "importance factors" suggest that the presence of these factors contributes minimally or decreases the predicted values of the dependent variable. Therefore, in our study, negative SHAP values for N_2O_5 during the daytime indicate that the contribution of N_2O_5 chemistry to daytime $ClNO_2$ levels was limited. We have added these discussions.

Added/rewritten: "Generally, negative "importance factors" suggest that the presence of these factors contributes minimally or decreases the predicted values of the dependent variable. Therefore, in our study, negative SHAP values for N_2O_5 during the daytime indicate that the contribution of N_2O_5 chemistry to daytime $ClNO_2$ levels was limited."

4. Section 3.2: A discussion on the changes in aerosol content (particulate nitrate) and the effect on N_2O_5 uptake and $ClNO_2$ yield is absent. Such a discussion is critical here. Traditionally, one expects nitrate to reduce N_2O_5 uptake (the nitrate effect) which would limit the production of $ClNO_2$. Even so, $ClNO_2$ could be enhanced in a high nitrate case if the N_2O_5 uptake and $ClNO_2$ yield are substantially greater than low nitrate air masses. According to Figure 1, there are concurrent enhancements of pCl and pNO_3 during some time periods. As pCl increases the $ClNO_2$ yield will also increase which would

then be (coincidentally?) concurrent with high pNO_3 Even more, these periods of concurrent pCl and pNO_3 appear to correlate with enhanced $PM_{2.5}$ and thus, I assume, aerosol surface area. Increases in surface area would then increase N_2O_5 uptake further promoting $ClNO_2$ and pNO_3 production. Lastly, Figure 6 suggests that the correlation between $ClNO_2$ mixing ratio and pNO_3xjNO_2xSa is driven by pNO_3xSa while jNO_2 has a limited or no correlation (panel d). In other words, photolysis appears to have a limited role in the production of $ClNO_2$.

While the above may be speculative, it is an example of why a lack of discussion on the $ClNO_2$ yield and N_2O_5 uptake significantly weakens the arguments made by the authors. As written, I believe there is insufficient evidence to conclude that "NO_3^- photolysis contributed to daytime [$ClNO_2$] generation".

Response: Thanks for your valuable comments. The N_2O_5 uptake coefficient ($\gamma(N_2O_5)$) and $ClNO_2$ yield ($\phi(ClNO_2)$) were estimated using the observational data and parameterization. We derived the values of $\phi(ClNO_2)$ based on increased rates of $ClNO_2$ and particle nitrate (NO_3^-) in the field observation (Phillips et al., 2016). Specially, $\gamma(N_2O_5)$ and $\phi(ClNO_2)$ were calculated by Eq. (1) and (2).

$$\gamma(N_2O_5) = \frac{2 \times \left(P(ClNO_2) + P(NO_3^-)\right)}{cN_2O_5 S_a [N_2O_5]} \quad (1)$$

$$\phi(ClNO_2) = 2 \times \left(1 + \frac{P(NO_3^-)}{P(ClNO_2)}\right)^{-1} \quad (2)$$

Here, $P(ClNO_2)$ and $P(NO_3^-)$ represent the production rates of $ClNO_2$ and NO_3^- induced by N_2O_5 uptake, respectively. S_a denotes the aerosol surface area, and $c(N_2O_5)$ is the mean molecular speed of N_2O_5. This method assumes that air masses remain relatively stable, and $ClNO_2$ and NO_3^- were produced through nighttime N_2O_5 heterogeneous uptake. More details on the method are provided elsewhere (Tham et al., 2018; Niu et al., 2022; Phillips et al., 2016). Using the method and selection criteria, we derived $\gamma(N_2O_5)$ and $\phi(ClNO_2)$ during the whole measurement period.

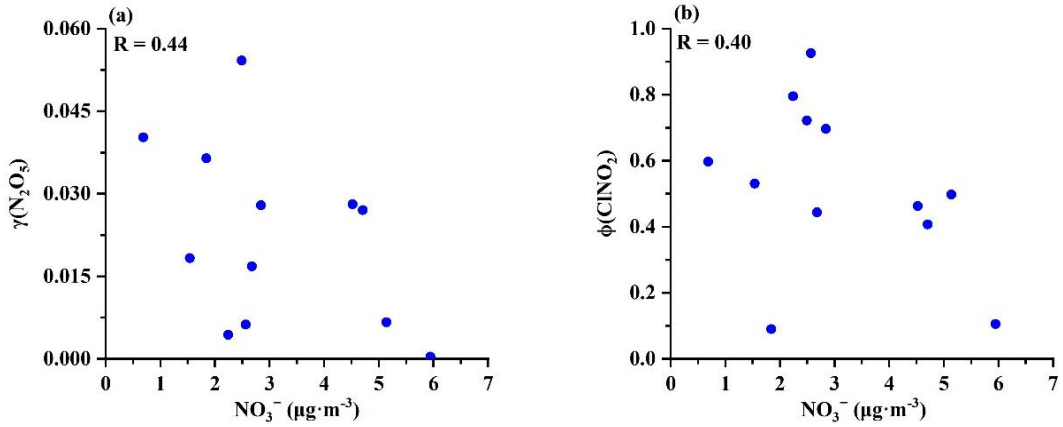

Figure R1. The relationship between field-derived $\gamma(N_2O_5)$ (a), $\phi(ClNO_2)$ (b) and NO_3^- concentrations.

The relative importance of NO_3^- derived from the XGBoost-SHAP result indicated that elevated $ClNO_2$ concentrations were associated with high concentrations of NO_3^- besides N_2O_5. High NO_3^- concentrations (> 3.7 $\mu g \cdot m^{-3}$) are accompanied by the elevation of $ClNO_2$, especially its concentrations reaching 6.2 $\mu g \cdot m^{-3}$. Previous studies suggested that the increased concentrations of NO_3^- decreased $\gamma(N_2O_5)$, which would limit the production of $ClNO_2$ (Wahner et al., 1998; Mentel et al., 1999; Bertram and Thornton, 2009). As depicted in Figure R1, the dependence of $\gamma(N_2O_5)$ on NO_3^- concentrations follows the nitrate suppression effect. Therefore, the importance of nighttime NO_3^- for $ClNO_2$ levels is that they are co-products from the processes of N_2O_5 heterogeneous uptake. During our filed observation, compared to low NO_3^- conditions, $ClNO_2$ production was enhanced in high NO_3^- conditions. Especially in late autumn, increased aerosol abundances and N_2O_5 levels enhanced N_2O_5 uptake, which further promoted both $ClNO_2$ and NO_3^- production.

To evaluate the contribution of the heterogeneous N_2O_5 uptake to daytime $ClNO_2$ levels, we calculated $ClNO_2$ production using Eq. (3), considering the loss of $ClNO_2$ through photolysis. This method has been employed in a previous study (Tham et al., 2016).

$$\frac{d[ClNO_2]}{dt} = k(N_2O_5)[N_2O_5]\phi(\mathrm{ClNO_2}) - JClNO_2[\mathrm{ClNO_2}] \qquad (3)$$

$$k(N_2O_5) = \frac{1}{4} cN_2O_5 S_a \gamma(N_2O_5) \quad (4)$$

We used a $\gamma(N_2O_5)$ value of 0.06 and a $\phi(ClNO_2)$ value of 1.0 in our calculations, which represented upper-end estimates based on previous field studies (Mcduffie et al., 2018a; Mcduffie et al., 2018b; Tham et al., 2016). However, as shown in Figure R2, a $\phi(ClNO_2)$ of 1.0 with a $\gamma(N_2O_5)$ of 0.06 ($\phi\gamma$ = 0.06) fails to reproduce the observed levels of daytime $ClNO_2$. A larger $\gamma(N_2O_5)$ of 0.11 would be necessary, but such high uptake coefficients and yields are not supported by the current literature. Therefore, we believe that the observed daytime $ClNO_2$ levels, particularly around noon, cannot be adequately explained by heterogeneous N_2O_5 uptake alone, suggesting the presence of additional sources contributing to the formation of daytime $ClNO_2$.

Notably, the laboratory research had confirmed that NO_3^- photolysis can produce $ClNO_2$ (Dalton et al., 2023). In our study, machine learning analysis, which gauges the "importance" of NO_3^- in affecting daytime $ClNO_2$, as well as a linear regression of $ClNO_2$ against $NO_3^- \times JNO_2 \times S_a$, implied that NO_3^- photolysis contributed to daytime $ClNO_2$ concentrations at our study site. Although NO_3^- photolysis can produce $ClNO_2$, this does not necessarily mean that higher photolysis intensity will result in higher $ClNO_2$ concentrations. It is crucial to understand the dual role of photolysis intensity in determining daytime $ClNO_2$ levels. Photolysis can contribute to the generation of $ClNO_2$ by promoting NO_3^- photolysis, while also causing the rapid decomposition of $ClNO_2$. As reported in California (Mielke et al., 2013), reduced photolysis rates even increased daytime $ClNO_2$ levels by decreasing $ClNO_2$ loss through photolysis. Additionally, in real atmospheric conditions, several factors beyond photolysis influence NO_3^- photolysis, including NO_3^- concentrations and particulate chloride levels.

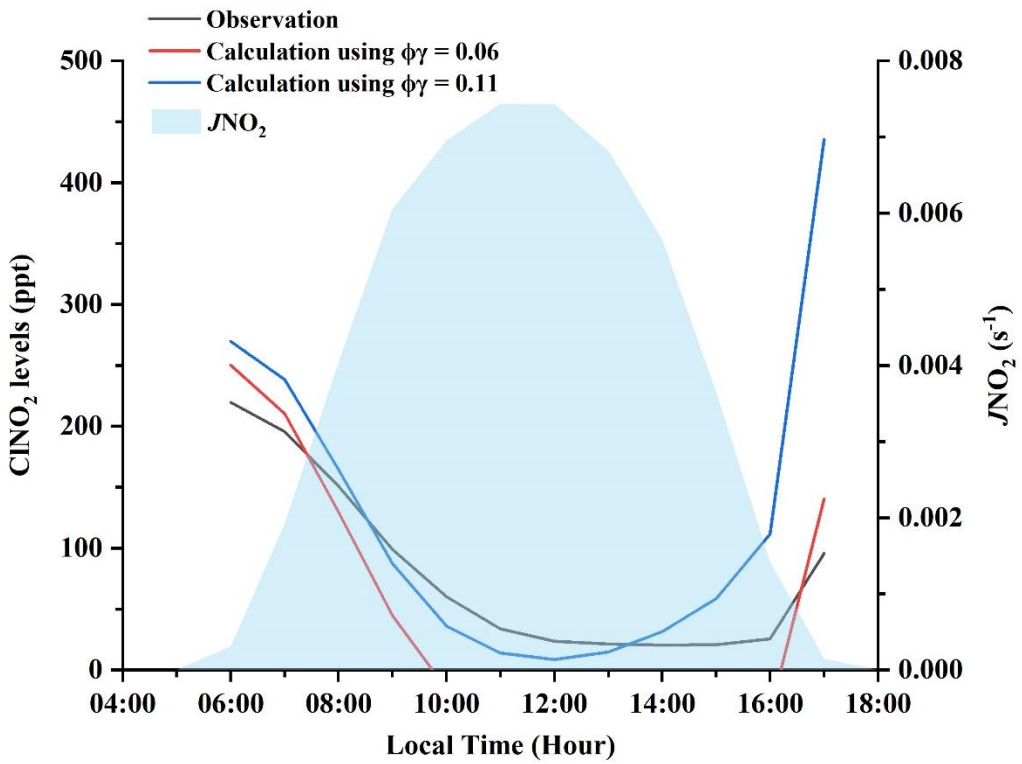

Figure R2. Comparisons of daytime $ClNO_2$ levels between observation, and calculation using Eq. (4) with a $\phi(ClNO_2)$ of 1.0 and a $\gamma(N_2O_5)$ of 0.06 ($\phi\gamma = 0.06$), or a $\phi(ClNO_2)$ of 1.0 and a $\gamma(N_2O_5)$ of 0.11 ($\phi\gamma = 0.11$).

Added/rewritten: "The average diurnal changes of $ClNO_2$ and related parameters during the entire measurement campaign are depicted in Fig. 2b. As expected, $ClNO_2$ exhibited a distinct diurnal variation, peaking and accumulating after sunset and decreasing in the early morning. However, $ClNO_2$ concentrations remained ~ 40 ppt around noon, different with some studies that $ClNO_2$ concentrations decreased to near the detection limit around midday (Wang et al., 2022; Niu et al., 2022). Similar observation in North China declared $ClNO_2$ concentrations above 60 ppt in the afternoon (Liu et al., 2017). Previous studies have indicated that abundant $ClNO_2$ may be transported from upper atmosphere or air mass, contributing to the elevated $ClNO_2$ concentrations in the early morning (Tham et al., 2016; Xia et al., 2021; Jeong et al., 2019). However, the explanations for the concentrations of $ClNO_2$ around noon remained elusive.

To evaluate the contribution of the heterogeneous N_2O_5 uptake to daytime $ClNO_2$

levels, we calculated $ClNO_2$ production using Eq. (S7), considering the loss of $ClNO_2$ through photolysis. This method has been employed in a previous study (Text S4-S5) (Tham et al., 2016). We used a $\gamma(N_2O_5)$ value of 0.06 and a $\phi(ClNO_2)$ value of 1.0 in our calculations, which represent upper-end estimates based on previous field studies (Mcduffie et al., 2018a; Mcduffie et al., 2018b; Tham et al., 2016). However, as shown in Fig. 3, the calculated $\phi(ClNO_2)$ with $\gamma(N_2O_5) = 0.06$ fails to reproduce the observed levels of daytime $ClNO_2$. A larger $\gamma(N_2O_5)$ of 0.11 would be necessary, but such high uptake coefficients and yields are not supported by the current literature. Therefore, we believe that the observed daytime $ClNO_2$ levels, particularly around noon, cannot be adequately explained by heterogeneous N_2O_5 uptake alone, suggesting the presence of additional sources contributing to the formation of daytime $ClNO_2$."

"Differently, the relative importance of NO_3^- derived from the XGBoost-SHAP result indicated that elevated $ClNO_2$ concentrations were associated with high concentrations of NO_3^- besides N_2O_5. According to Fig. 5b, high NO_3^- concentrations ($> 3.7\ \mu g \cdot m^{-3}$) are accompanied by the elevation of $ClNO_2$, especially its concentrations reaching $6.2\ \mu g \cdot m^{-3}$. Previous studies suggested that increased concentrations of NO_3^- decreased $\gamma(N_2O_5)$, which would limit the production of $ClNO_2$ (Wahner et al., 1998; Mentel et al., 1999; Bertram and Thornton, 2009). As depicted in Fig. R1, the dependence of $\gamma(N_2O_5)$ on NO_3^- concentrations follows the nitrate suppression effect. Therefore, the importance of nighttime NO_3^- for $ClNO_2$ levels is that they are co-products from the processes of N_2O_5 heterogeneous uptake. As shown in Fig. 1, compared to low NO_3^- conditions, $ClNO_2$ production was enhanced in high NO_3^- conditions. Especially in late autumn, increased aerosol abundances and N_2O_5 levels increased N_2O_5 uptake further promoting $ClNO_2$ and NO_3^- production."

"It is crucial to understand the dual role of photolysis intensity in determining daytime $ClNO_2$ levels. Photolysis can contribute to the generation of $ClNO_2$ by promoting NO_3^- photolysis, while also causing the rapid decomposition of $ClNO_2$. As reported in California (Mielke et al., 2013), reduced photolysis rates even increased daytime $ClNO_2$ levels by decreasing $ClNO_2$ loss through photolysis."

Technical Comments

Line 76: tenths: tens

Response: Thanks for your comment. We have revised it.

Added/rewritten: "Since Osthoff et al. (2008) firstly detected over 1 ppb of $ClNO_2$ in the urban outflows of America, significant production of $ClNO_2$ was widely observed in the polluted coastal and inland areas with abundant anthropogenic emissions and chloride sources, and its concentrations were ranged from tens of ppt to several ppb."

Figure 3, 5 and 6: Please change the color scale to a colorblind friendly version.

Response: Thanks for your comment. We have changed the color scale in Figure 3, 5 and 6 to a colorblind friendly version. Additionally, due to N_2O_5, NO_3^-, T, RH, and UV being the most important features of affecting $ClNO_2$ concentrations, we only compared their relative importance. Therefore, Figure 5 only presents the relative importance of N_2O_5, NO_3^-, T, RH, and UV.

Added/rewritten:

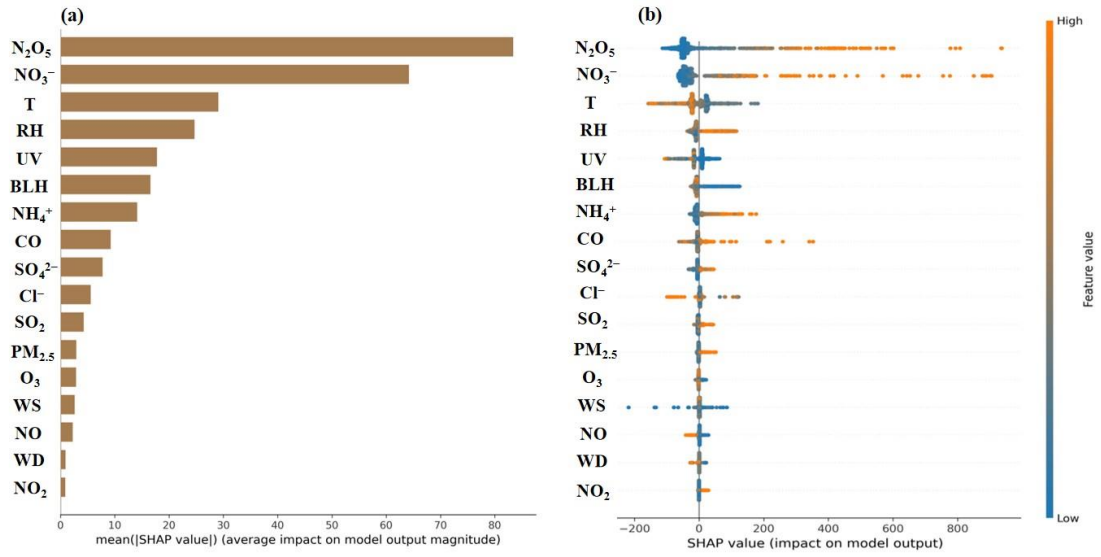

Figure 3. Relative importance of each feature to $ClNO_2$ using XGBoost-SHAP during the autumn observation period. The mean absolute SHAP value (a), summary plot of SHAP values of each feature (b).

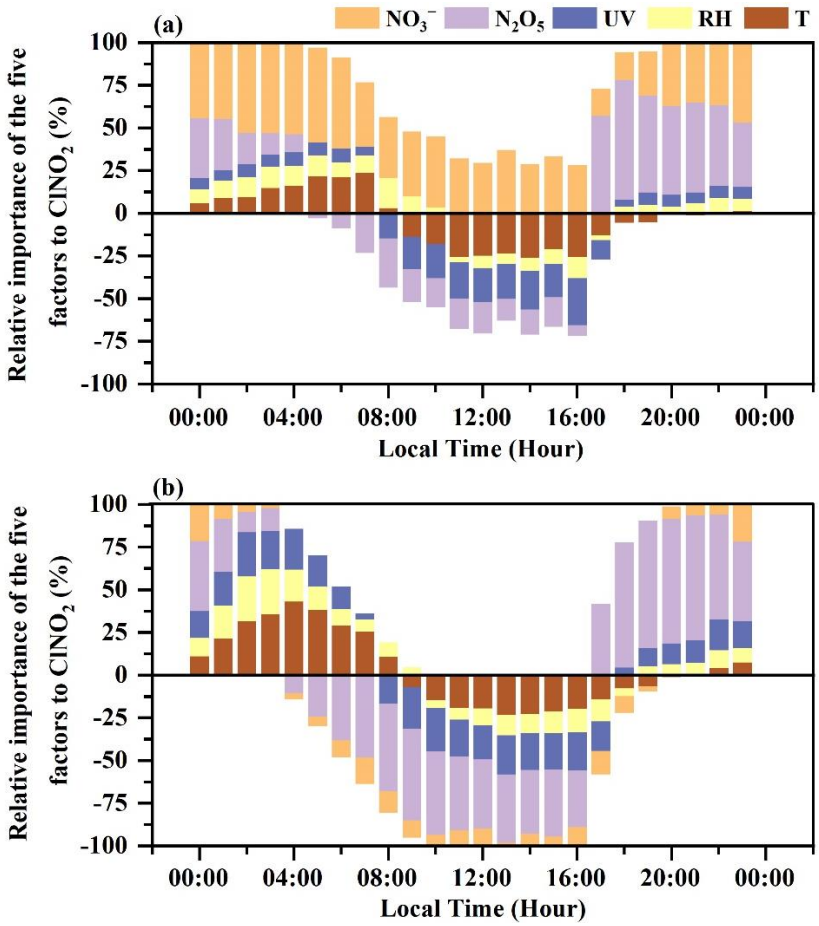

Figure 5. The diurnal variations of the relative importance of the major five factors (including N_2O_5, NO_3^-, T, RH, and UV) to $ClNO_2$ based on the SHAP values under the high (> 3.7 μg·m^{-3}) (a) and low (< 3.7 μg·m^{-3}) (b) $ClNO_2$ concentrations.

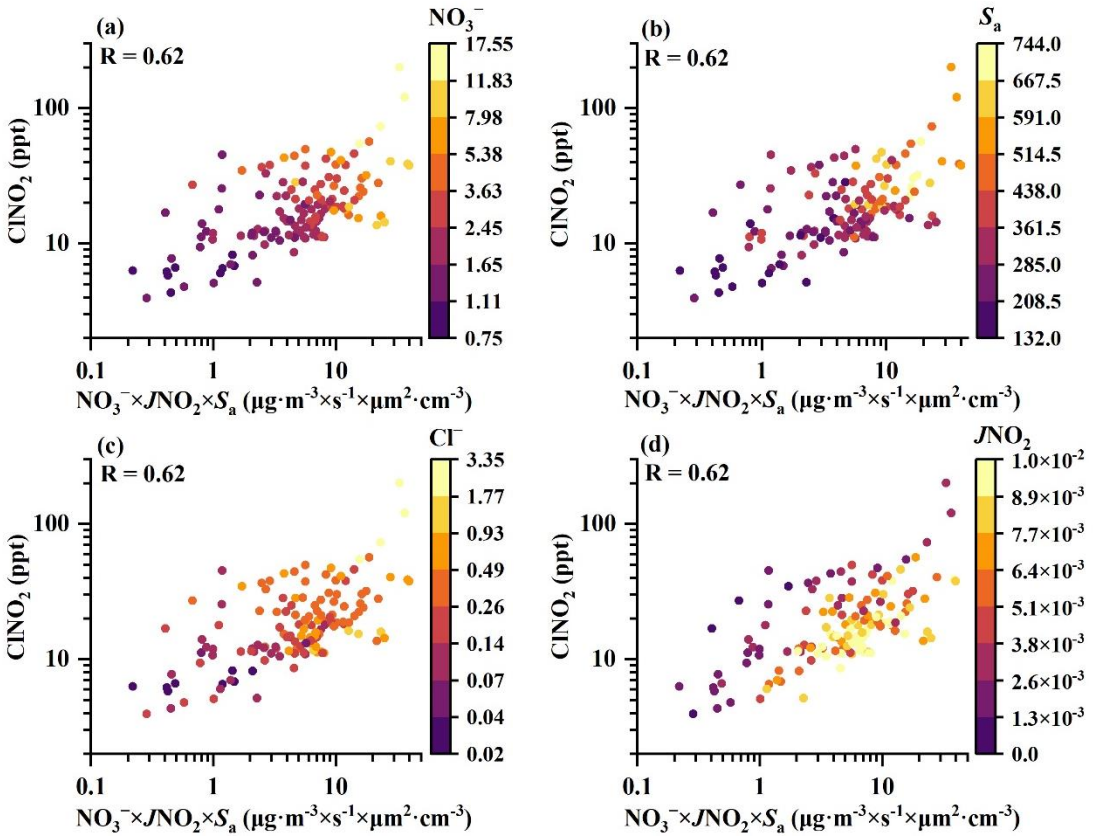

Figure 6. The relationship of daytime $ClNO_2$ concentrations (12:00-15:00 Local Time) and a proxy of nitrate (NO_3^-) photolysis ($NO_3^-\times JNO_2\times S_a$). The color of the dots denotes the NO_3^- (a), S_a (b), Cl^- (c), JNO_2 (d), respectively.

Line 215: averagely: average

Response: Thanks for your comment. We have corrected it.

Added/rewritten: "Therefore, the average daily concentrations of NO_3^- were classified as high (> 3.7 $\mu g\cdot m^{-3}$) and low (< 3.7 $\mu g\cdot m^{-3}$) NO_3^- cases to further elucidate the impacts of NO_3^- on the formation of $ClNO_2$."

Line 224: corrected: correlated

Response: Thanks for your comment. We have revised it.

Added/rewritten: "As depicted in Figure 6, it is observed that daytime $ClNO_2$ concentrations correlated well (R = 0.62) with the product of a proxy of NO_3^- photolysis ($NO_3^-\times JNO_2\times S_a$) on aerosol surfaces ($S_a$), implying that the photolysis of NO_3^- contributed to the daytime concentrations of $ClNO_2$ at our study site."

References

Bertram, T. and Thornton, J.: Toward a general parameterization of N_2O_5 reactivity on aqueous particles: the competing effects of particle liquid water, nitrate and chloride, Atmos. Chem. Phys., 9, 8351-8363, https://doi.org/10.5194/acp-9-8351-2009, 2009.

Dalton, E. Z., Hoffmann, E. H., Schaefer, T., Tilgner, A., Herrmann, H., and Raff, J. D.: Daytime Atmospheric Halogen Cycling through Aqueous-Phase Oxygen Atom Chemistry, J. Am. Chem. Soc., 145, 15652-15657, https://doi.org/10.1021/jacs.3c03112, 2023.

Jeong, D., Seco, R., Gu, D., Lee, Y., Nault, B. A., Knote, C. J., McGee, T., Sullivan, J. T., Jimenez, J. L., Campuzano-Jost, P., Blake, D. R., Sanchez, D., Guenther, A. B., Tanner, D., Huey, L. G., Long, R., Anderson, B. E., Hall, S. R., Ullmann, K., Shin, H., Herndon, S. C., Lee, Y., Kim, D., Ahn, J., and Kim, S.: Integration of airborne and ground observations of nitryl chloride in the Seoul metropolitan area and the implications on regional oxidation capacity during KORUS-AQ 2016, Atmos. Chem. Phys., 19, 12779-12795, https://doi.org/10.5194/acp-19-12779-2019, 2019.

Liu, X., Qu, H., Huey, L. G., Wang, Y., Sjostedt, S., Zeng, L., Lu, K., Wu, Y., Hu, M., Shao, M., Zhu, T., and Zhang, Y.: High Levels of Daytime Molecular Chlorine and Nitryl Chloride at a Rural Site on the North China Plain, Environ. Sci. Technol., 51, 9588-9595, https://doi.org/10.1021/acs.est.7b03039, 2017.

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.: $ClNO_2$ Yields From Aircraft Measurements During the 2015 WINTER Campaign and Critical Evaluation of the Current Parameterization, J. Geophys. Res. Atmos., 123, 12,994-913,015, https://doi.org/10.1029/2018JD029358, 2018a.

McDuffie, E. E., Fibiger, D. L., Dubé, W. P., Lopez-Hilfiker, F., Lee, B. H., Thornton, J. A., Shah, V., Jaeglé, L., Guo, H., Weber, R. J., Michael Reeves, J., 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., Hornbrook, R. S., Apel, E. C., Campos, T., Hall, S. R., Ullmann, K., and Brown, S. S.: Heterogeneous N_2O_5 Uptake During Winter: Aircraft Measurements During the 2015 WINTER Campaign and Critical Evaluation of Current Parameterizations, J. Geophys. Res. Atmos., 123, 4345-4372, https://doi.org/10.1002/2018JD028336, 2018b.

Mentel, T. F., Sohn, M., and Wahner, A. J. P. C. C. P.: Nitrate effect in the heterogeneous hydrolysis of dinitrogen pentoxide on aqueous aerosols, Phys. Chem. Chem. Phys., 1, 5451-5457, https://doi.org/10.1039/A905338g, 1999.

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., 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 NO_x reservoir species during CalNex-LA 2010, J. Geophys. Res. Atmos., 118, 10,638-610,652, https://doi.org/10.1002/jgrd.50783, 2013.

Niu, Y.-B., Zhu, B., He, L.-Y., Wang, Z., Lin, X.-Y., Tang, M.-X., and Huang, X.-F.: Fast Nocturnal Heterogeneous Chemistry in a Coastal Background Atmosphere and Its Implications for Daytime Photochemistry, J. Geophys. Res. Atmos., 127, e2022JD036716, https://doi.org/10.1029/2022JD036716, 2022.

Phillips, G. J., Thieser, J., Tang, M., Sobanski, N., Schuster, G., Fachinger, J., Drewnick, F., Borrmann, S., Bingemer, H., Lelieveld, J., and Crowley, J. N.: Estimating N_2O_5 uptake coefficients using ambient measurements of NO_3, N_2O_5, $ClNO_2$ and particle-phase nitrate, Atmos. Chem. Phys., 16, 13231-13249, https://doi.org/10.5194/acp-16-13231-2016, 2016.

Tham, Y. J., Wang, Z., Li, Q., Wang, W., Wang, X., Lu, K., Ma, N., Yan, C., Kecorius, S., Wiedensohler, A., Zhang, Y., and Wang, T.: Heterogeneous N_2O_5 uptake coefficient and production yield of $ClNO_2$ in polluted northern China: roles of

aerosol water content and chemical composition, Atmos. Chem. Phys., 18, 13155-13171, https://doi.org/10.5194/acp-18-13155-2018, 2018.

Tham, Y. J., Wang, Z., Li, Q., Yun, H., Wang, W., Wang, X., Xue, L., Lu, K., Ma, N., Bohn, B., Li, X., Kecorius, S., Größ, J., Shao, M., Wiedensohler, A., Zhang, Y., and Wang, T.: Significant concentrations of nitryl chloride sustained in the morning: investigations of the causes and impacts on ozone production in a polluted region of northern China, Atmos. Chem. Phys., 16, 14959-14977, https://doi.org/10.5194/acp-16-14959-2016, 2016.

Wahner, A., Mentel, T. F., Sohn, M., and Stier, J.: Heterogeneous reaction of N_2O_5 on sodium nitrate aerosol, J. Geophys. Res. Atmos., 103, 31103-31112, https://doi.org/10.1029/1998JD100022, 1998.

Wang, H., Yuan, B., Zheng, E., Zhang, X., Wang, J., Lu, K., Ye, C., Yang, L., Huang, S., and Hu, W.: Formation and impacts of nitryl chloride in Pearl River Delta, Atmos. Chem. Phys., 22, 14837-14858, https://doi.org/10.5194/acp-22-14837-2022, 2022.

Xia, M., Peng, X., Wang, W., Yu, C., Wang, Z., Tham, Y. J., Chen, J., Chen, H., Mu, Y., and Zhang, C.: Winter $ClNO_2$ formation in the region of fresh anthropogenic emissions: seasonal variability and insights into daytime peaks in northern China, Atmos. Chem. Phys., 21, 15985-16000, https://doi.org/10.5194/acp-21-15985-2021, 2021.

RC2: 'Comment on egusphere-2024-1638', Anonymous Referee #3, 03 Jan 2025

In this manuscript, the authors present a study that investigates key factors driving the production of $ClNO_2$ based on field observations and XGBoost-SHAP model. Furthermore, the authors evaluated the potential impact of $ClNO_2$ photolysis on the formation of RO_2 and hence, the atmospheric oxidative capacity.

Overall, I found this manuscript interesting and well-constructed. Although the conclusion drawn for the nighttime $ClNO_2$ formation has been well recognized for two decades, the contribution of NO_3^- photolysis to daytime $ClNO_2$ is confirmed by the authors, which brings sufficient novelty to this manuscript.

Despite this, I do have some comments, particularly on the interpretation of the machine learning results, which need to be fully addressed before this manuscript can be accepted for publication.

Response: Thank you for your valuable and thoughtful comments. Your comments and suggestions have greatly enhanced the overall quality and readability of the manuscript. We have made the necessary revisions and provided detailed responses to each point below for your consideration.

General comments:

1. Machine learning, especially SHAP value, starts to be widely used in atmospheric research very recently, but many readers may not be sufficiently familiar with it. To improve the readability, I believe the way of interpreting SHAP values must be fully informed in the manuscript. E.g., what do the negative and positive SHAP values stand for? Should the contribution be evaluated by the true value or absolute value.

Response: Thank you for your comment. We have added a detailed introduction to SHAP values in the revised manuscript.

Added/rewritten: "The SHAP model is an interpretability tool designed to analyze the contributions of individual features to model predictions. It employs an additive explanatory framework that considers all features as contributors, drawing inspiration from cooperative game theory. For each predicted instance, SHAP assigns

a Shapley value, representing the cumulative contribution of each feature. Positive SHAP values indicate that a feature increases the model's predicted outcome, signifying a positive contribution. Conversely, negative SHAP values suggest that the feature reduces the predicted value, reflecting a negative contribution. The absolute value of the SHAP score reflects the magnitude of the contribution, regardless of direction, offering insight into the overall importance of the feature. The true value, on the other hand, reveals the direction of the contribution (positive or negative), facilitating a clearer understanding of the relationship between the feature and the prediction."

2. I am not fully convinced by the way of performing SHAP model and its interpretation.

1) why does the aerosol surface, as a known important factor for N_2O_5 uptake, not used as an input of SHAP model?

Response: Thank you for your valuable comment. We agree that aerosol surface area is a crucial factor influencing the heterogeneous uptake of N_2O_5. Initially, we had included particle surface area concentrations (S_a) in the XGBoost-SHAP model to assess its significance in $ClNO_2$ formation. However, the results indicated that S_a did not play a prominent role (Figure R3). Furthermore, it is found that R^2 values of the training and testing sets slightly improved from 0.963 and 0.861 to 0.965 and 0.891, respectively, when S_a was not used as an input of a machine learning model. Given that $PM_{2.5}$ and its inorganic compositions serve as representative indicators of aerosol conditions to some extent, we chose not to include aerosol surface area as a dependent variable in the machine learning model to avoid redundancy.

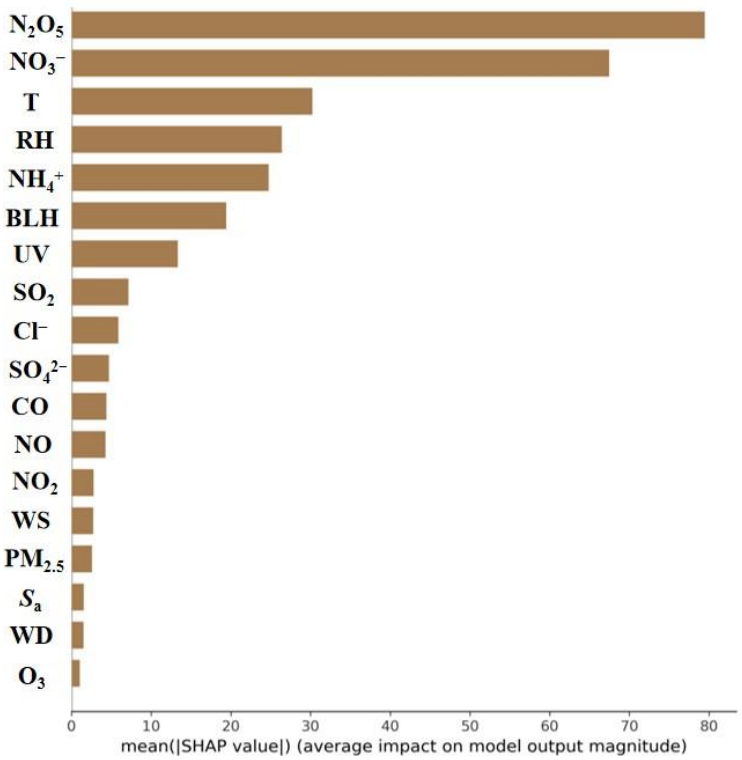

Figure R3. Relative importance of each feature to $ClNO_2$ using the XGBoost-SHAP model during the autumn observation period, with S_a included as an additional variable in the model.

2) $ClNO_2$ has a rather long nighttime lifetime, which means $ClNO_2$ could be accumulated during airmass transport. Meanwhile, N_2O_5 could both form and loss through the transport, leading to varying patterns of its concentration. In fact, this can be testified by calculating the maximal $ClNO_2$ production through N_2O_5 uptake by, e.g., assuming gamma = 0.1 and $ClNO_2$ yield = 1. Given this assumption, I didn't see any model input that could represent the influence of airmass transport. I suggest to reconsider their model input and incorporate certain transport parameters.

Response: Thank you for your thoughtful comment. I fully agree with your opinion that $ClNO_2$ tends to accumulate at night. We had indeed considered the impact of air mass transport in our analysis. In this study, trace gases (SO_2, CO, NO_2, NO, O_3, and N_2O_5), $PM_{2.5}$ and its inorganic compositions (NO_3^-, SO_4^{2-}, NH_4^+, and Cl^-), along with meteorological parameters (T, RH, UV, WS, WD, and BLH) were selected as independent variables. Typically, WS and WD effectively reflect

the influence of air masses and play a significant role in the transport, dispersion, and accumulation of atmospheric pollutants. However, results from the XGBoost-SHAP model indicate that WS and WD have a minimal impact on $ClNO_2$ concentrations (Figure R4). Notably, previous observations indicating that $ClNO_2$ is easily influenced by air mass transport were primarily conducted in clean rural areas or under background atmospheric conditions (Niu et al., 2022; Tan et al., 2022). Given that our study site located in a typical urban area surrounded by shopping malls, residential zones, and major traffic arteries, it is highly affected by fresh anthropogenic emissions. Therefore, these results suggest that $ClNO_2$ concentrations are primarily driven by local processes, rather than by air mass transport during our study period.

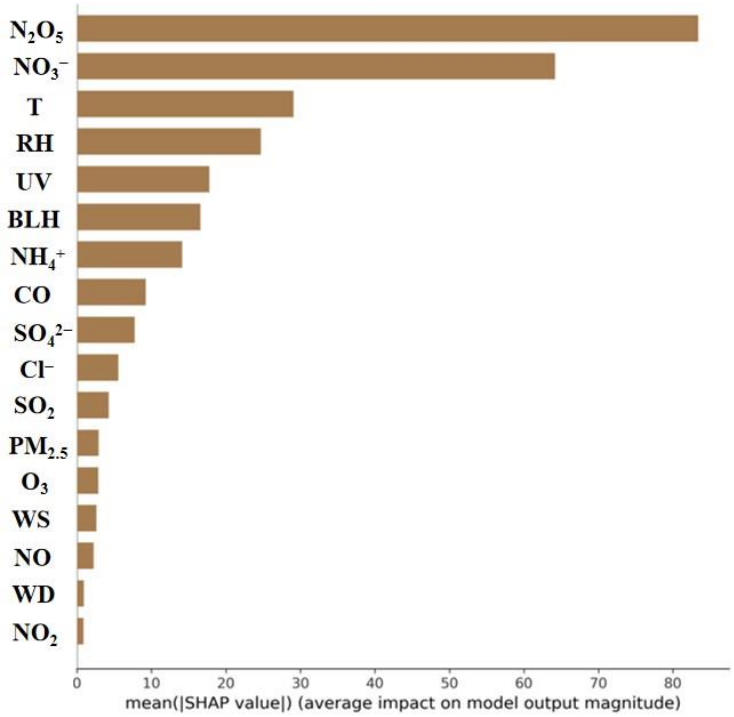

Figure R4. Relative importance of each feature to $ClNO_2$ using the XGBoost-SHAP model during the autumn observation period.

3) As this study suggested, daytime and nighttime $ClNO_2$ are driven by different processes, which however, were affected by similar parameters (in different ways). For instance, NO_3^- is a co-product with $ClNO_2$ at nighttime, but a precursor of $ClNO_2$ in the daytime. I suggest to consider conducting SHAP models daytime and

nighttime data sets separately, so that the exact role of these parameters can be better revealed.

Response: Thanks for your constructive comment. We fully agree with your insightful perspective. Through our in-depth analysis, we found that $ClNO_2$ exhibits distinctly different influence pathways during the daytime and nighttime, with certain parameters potentially playing different roles in these two periods. To investigate this further, we integrated all daytime and nighttime data into a unified machine learning model, resulting in a high-performing model. Using SHAP analysis, we were able to effectively distinguish the roles of key influencing factors between daytime and nighttime.

While the primary formation mechanisms of $ClNO_2$ differ between daytime and nighttime, there is a clear interconnection between daytime and nighttime $ClNO_2$ concentrations. Especially, the elevated nighttime $ClNO_2$ concentrations can significantly affect its concentrations in the early morning. Machine learning models trained exclusively on daytime data show poor performance, with R^2 values for the testing sets dropping below 0.6, thereby constraining further analysis of factor importance. As a result, separating daytime and nighttime data for independent machine learning analyses may risk overlooking the intrinsic linkages between these periods.

We believe that a comprehensive analysis, incorporating both daytime and nighttime data, is crucial for a complete and accurate assessment of $ClNO_2$ production and loss processes. Although we did not segregate the data into daytime and nighttime subsets for machine learning, SHAP analysis enabled us to clearly identify the relative importance of various factors during the daytime and nighttime, providing deeper insights into their respective mechanisms across these two periods.

For example, we used SHAP analysis to evaluate the key influencing factors of daytime $ClNO_2$. The simulated concentrations of $ClNO_2$, based on the XGBoost-SHAP model, were significantly elevated when NO_3^- concentrations were higher than 3.7 $\mu g \cdot m^{-3}$. Consequently, the average daily concentrations of NO_3^- were classified as high (> 3.7 $\mu g \cdot m^{-3}$) and low (< 3.7 $\mu g \cdot m^{-3}$) to further elucidate the impacts of NO_3^- on the formation of $ClNO_2$. Fig. R5 presents the diurnal variations in the relative importance

of the most critical influencing factors based on the SHAP values under high and low NO_3^- concentrations. Unexpectedly, daytime NO_3^- was the dominant influencing factors for daytime $ClNO_2$ (Fig. R5a). High concentrations of daytime NO_3^- positively affected the daytime concentrations of $ClNO_2$, independent of N_2O_5 uptake processes. As depicted in Fig. R5a, daytime N_2O_5 did not promote the elevation of daytime $ClNO_2$. Negative SHAP values for N_2O_5 during the daytime indicate that the contribution of N_2O_5 chemistry to daytime $ClNO_2$ levels was limited. Therefore, it is very likely that high concentrations of daytime NO_3^- participated in daytime $ClNO_2$ production.

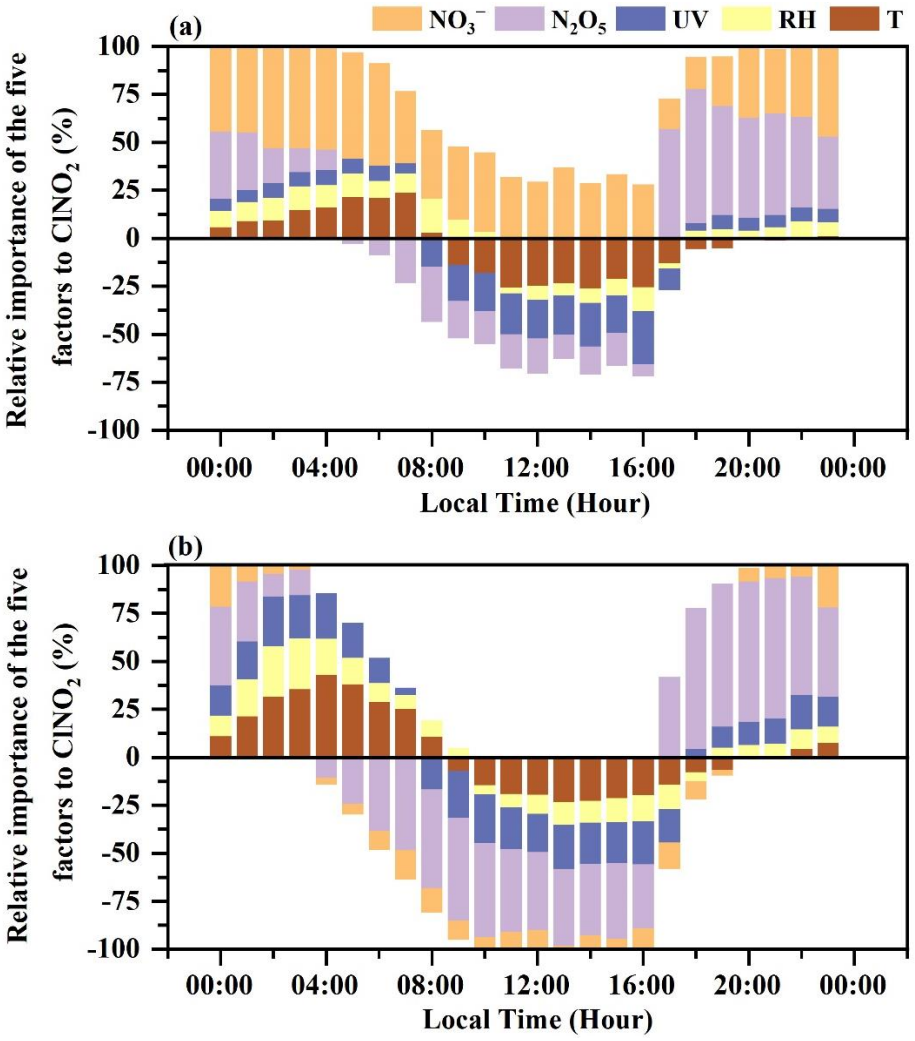

Figure R5. The diurnal variations of the relative importance of factors to $ClNO_2$ based on the SHAP values under the high (> 3.7 $\mu g \cdot m^{-3}$) (a) and low (< 3.7 $\mu g \cdot m^{-3}$) (b) $ClNO_2$ concentrations.

Detailed comments:

Line 64 “were” could be replaced by “are”, as this is common case.

Response: Thanks for your comment. We have revised it.

Added/rewritten: “The reaction rates between Cl radical and some alkanes are several orders of magnitude faster than those involving OH radical.”

Line 99-100 “our research integrated….” This sentence has grammatic error, please rephrase.

Response: Thanks for your comment. This sentence has been rephrased.

Added/rewritten: “Field observations, combined with a machine learning model, were used to reveal the key driving factors of $ClNO_2$ formation. Furthermore, we further investigated the potential mechanisms driving daytime $ClNO_2$ generation.”

Line 141-143. The statement of $JClNO_2$ calculation is not clear, please consider to rephrase.

Response: Thanks for your comment. The statement of $JClNO_2$ calculation has been rephrased.

Added/rewritten: “The Tropospheric Ultraviolet and Visible Radiation (TUV) model was used to calculate $ClNO_2$ photolysis rates ($JClNO_2$) under clear-sky conditions. The simulated $JClNO_2$ values were then scaled based on field-measured JNO_2 values.”

Line 167-168 “Simultaneously, …” I think the high correlation between $ClNO_2$ and N_2O_5 (and NO_3^-) does not mean simultaneous peaking. From Fig.1, I can clearly see that their concentrations do not reach the maxima at exactly the same time.

Response: Thanks for your valuable comment. We agree with your opinion that the concentrations of $ClNO_2$, N_2O_5, and NO_3^- did not reach their maxima simultaneously. We intended to convey that their peak concentrations were observed during the night of November 27th. The sentences have been revised accordingly.

Added/rewritten: “The highest concentrations of $ClNO_2$ were detected during the

night of November 27th, with a maximum hourly average of 3.4 ppb. Peak concentrations of N_2O_5 and NO_3^- were also observed on that night."

Line 203-204 the authors first indicate NO_3^- could affect the formation of $ClNO_2$; but afterwards, the authors say that the high NO_3^- and $ClNO_2$ together were caused by the simultaneous formation. Please improve the logic of this part.

Response: Thanks for your comment. We have improved the logic of this part.

Added/rewritten: "Differently, the relative importance of NO_3^- derived from the XGBoost-SHAP result indicated that elevated $ClNO_2$ concentrations were associated with high concentrations of NO_3^- besides N_2O_5. According to Fig. 5b, high NO_3^- concentrations (> 3.7 $\mu g \cdot m^{-3}$) are accompanied by the elevation of $ClNO_2$, especially its concentrations reaching 6.2 $\mu g \cdot m^{-3}$. The importance of nighttime NO_3^- for $ClNO_2$ levels is that they are co-products from the processes of N_2O_5 heterogeneous uptake. As shown in Fig. 1, compared to low NO_3^- conditions, $ClNO_2$ production was enhanced in high NO_3^- conditions."

Line 221 "did not promoted…" should be "did not promote".

Response: Thanks for your comment. We have revised it.

Added/rewritten: "As depicted in Fig. 5a, daytime N_2O_5 did not promote the elevation of daytime $ClNO_2$."

Line 222 "A recent study declared that…". Please use "suggested" or "argued" instead of "declared".

Response: Thanks for your comment. We have revised it.

Added/rewritten: "A recent study suggested that nitrate photolysis produced $ClNO_2$ in addition to Cl_2 (Dalton et al., 2023), while it has been not verified by field observations."

Line 236-237. I am not convinced by the discussion about the role of temperature. The authors suggested that N_2O_5 is not important for $ClNO_2$ in the daytime. Then how can

temperature affect $ClNO_2$ through the thermal equilibrium of N_2O_5? Also, N_2O_5 is a measured quantity. Such a temperature impact should be already reflected by the connection between daytime N_2O_5 and $ClNO_2$.

Response: Thank you for your comments. We believe that N_2O_5 plays a critical role in the formation of $ClNO_2$, as $ClNO_2$ is generated through the heterogeneous uptake of N_2O_5 on chloride-containing aerosols. In this study, we emphasized that limited contribution of heterogeneous N_2O_5 uptake to daytime $ClNO_2$ concentrations was primarily due to very low daytime N_2O_5 levels, which are largely associated with its thermal decomposition. In other words, the thermal decomposition process affects $ClNO_2$ generation by reducing the availability of N_2O_5 in the daytime. Specifically, the elevated ambient temperature from nighttime to daytime reduced N_2O_5 concentrations through enhanced thermal decomposition. During the entire observation period from October to November, the overall drop in ambient temperature facilitated $ClNO_2$ production by reducing the thermal decomposition of N_2O_5, thereby increasing its availability for heterogeneous uptake.

Added/rewritten: "The impact of ambient temperature on $ClNO_2$ was probably reflected in its thermal equilibrium with N_2O_5. Elevated daytime ambient temperature suppressed the formation of N_2O_5, resulting in low N_2O_5 concentrations, which further limited the contribution of heterogeneous N_2O_5 uptake to daytime $ClNO_2$ generation. During the whole observation period from October to November, the drop in ambient temperature facilitated $ClNO_2$ production by decreasing the thermal decomposition process."

Line 243 I suggest the subtitle of "Impact of $ClNO_2$ photolysis on RO_x budget"

Response: Thanks for your suggestion. We have revised it.

Added/rewritten: "3.3 Impact of $ClNO_2$ photolysis on RO_x budget."

Figure 2: the N_2O_5 in the lowest panel is barely seen. Please consider to show the pattern by perhaps N_2O_5*5.

Response: Thank you for your suggestion. We have revised Figure 2 to update the

presentation of N_2O_5 accordingly.

Added/rewritten:

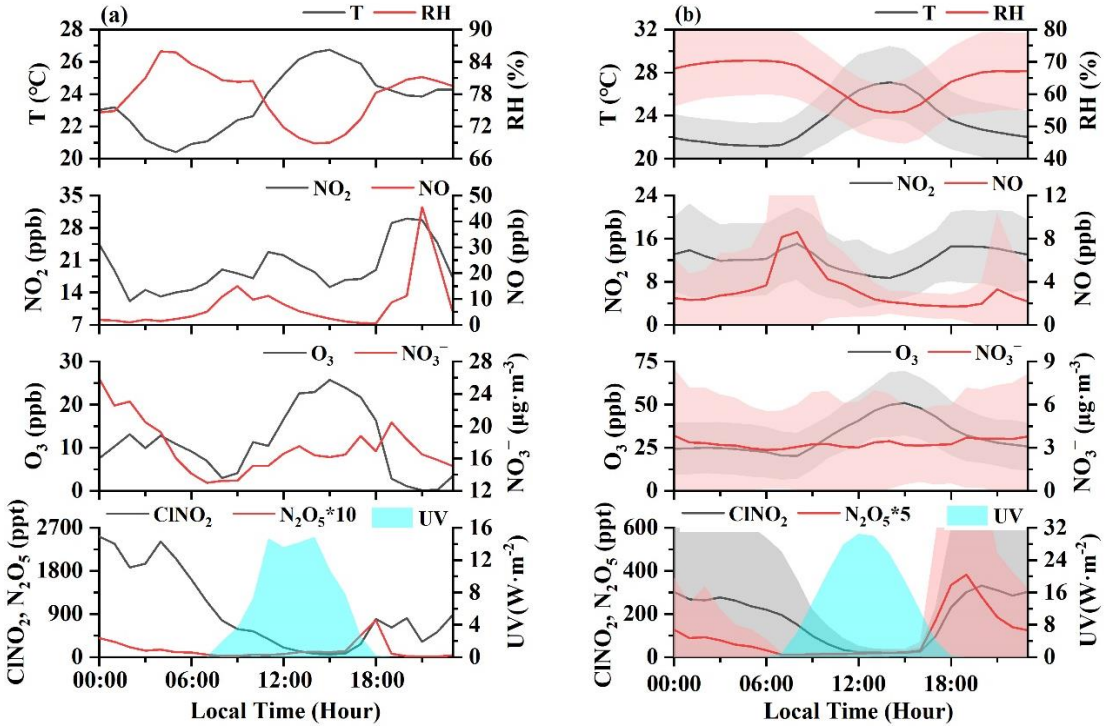

Figure 2. Diurnal variations of $ClNO_2$ and other related parameters for the highest concentrations of $ClNO_2$ (case) on November 28th (a) and the observation-average condition (from 9 October to 5 December) (b).

Figure 4. the division of x ticks looks strange. Please modify.

Response: Thanks for your comment. We have modified Figure 4.

Added/rewritten:

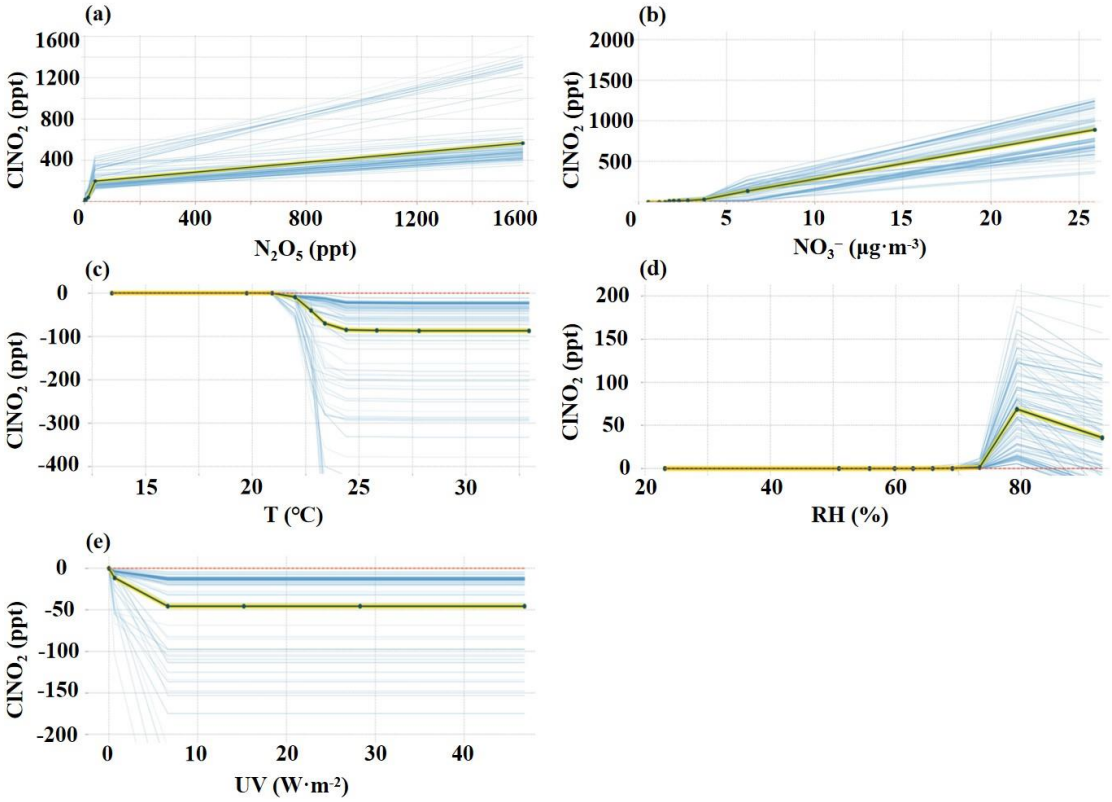

Figure 4. Isolation plots of PDP for N_2O_5 (a), NO_3^- (b), T (c), RH (d), and UV (e). The average variations of simulated $ClNO_2$ with factors' changes spline are indicated by the yellow and black curve, and blue curves presents all situations during the whole observation period.

References

Dalton, E. Z., Hoffmann, E. H., Schaefer, T., Tilgner, A., Herrmann, H., and Raff, J. D.: Daytime Atmospheric Halogen Cycling through Aqueous-Phase Oxygen Atom Chemistry, J. Am. Chem. Soc., 145, 15652-15657, https://doi.org/10.1021/jacs.3c03112, 2023.

Niu, Y.-B., Zhu, B., He, L.-Y., Wang, Z., Lin, X.-Y., Tang, M.-X., and Huang, X.-F.: Fast Nocturnal Heterogeneous Chemistry in a Coastal Background Atmosphere and Its Implications for Daytime Photochemistry, J. Geophys. Res. Atmos., 127, e2022JD036716, https://doi.org/10.1029/2022JD036716, 2022.

Tan, Z., Fuchs, H., Hofzumahaus, A., Bloss, W. J., Bohn, B., Cho, C., Hohaus, T., Holland, F., Lakshmisha, C., Liu, L., Monks, P. S., Novelli, A., Niether, D., Rohrer, F.,

Tillmann, R., Valkenburg, T. S. E., Vardhan, V., Kiendler-Scharr, A., Wahner, A., and Sommariva, R.: Seasonal variation in nitryl chloride and its relation to gas-phase precursors during the JULIAC campaign in Germany, Atmos. Chem. Phys., 22, 13137-13152, https://doi.org/10.5194/acp-22-13137-2022, 2022.