

Response to Editors and Reviewers

We appreciate the reviewers for their careful reading and constructive comments on our manuscript. As detailed below, the reviewer's comments are shown in black, our response to the comments is in blue. New or modified text is in red.

All the line numbers refer to Manuscript ID: acp-2022-408.

Referee 1

Wang et al., presented field measurements of N_2O_5 , ClNO_2 and related species at a rural site of South China. Comprehensive analysis is performed regarding the sources of particulate chloride and kinetic parameters like uptake coefficient and production yield. The authors also performed model simulation to evaluate the impacts of ClNO_2 on atmospheric oxidation capacity, although the impacts look minor during this observation period. The contents look rich and well fits into the scope of ACP. The methods are suitable and described with proper details. The results and conclusion are reasonable. However, the authors are suggested to show the highlight of this paper more clearly. Besides, the conclusion part can be more concise. The language polish is also necessary. Other issues are listed below. Overall, I would suggest a major revision.

Thanks for the review's constructive comments. We clarified the key highlights and shortened the conclusion accordingly. More details can be found in the following response in detail.

Major comments:

1. Many of the results presented here are within expectations or can be found in previous work. The authors are suggested to show the unique value of this work. One possible way is that the authors may make more detailed comparisons with previous field observations in China and abroad and demonstrate how the results exhibited here are different from previous studies and briefly discuss why.

We appreciate for the reviewer's suggestion to improve the value of our work. In the revised manuscript, we summarized the environmental impacts of ClNO_2 on the enhancement of ozone and radical formation to highlight the overall minor contribution of ClNO_2 chemistry to ozone formation and radical production on average conditions at different regions. Although some significant contributions from ClNO_2 chemistry were also observed in previous studies case by case.

In brief, we added a paragraph and a table to discuss the impacts and the reasons as follows.

Line 553. Table 6 summarized the observation-constrained box model simulation results about the impacts of ClNO_2 chemistry. The average ClNO_2 concentration in the observation is moderate compared with previous observations, other radical precursors (e.g., HCHO) also elevated at the same time. This leads to a large total radical and ozone production rate and a relatively minor contribution by ClNO_2 chemistry. This indicates that the contribution of ClNO_2 chemistry is indirectly affected by the budget of other radical precursors. In addition, a significant contribution by ClNO_2 chemistry to photochemical pollution was frequently observed in different campaigns (Tham et al., 2016; Wang et al., 2016), in which the receptor site may have aging plumes with higher ClNO_2 and thus larger contributions (Wang et al., 2016), suggests the large variability of ClNO_2 and its environmental impacts at various air masses. Here, our observations should be representative of the local condition and reflect the chemistry and impacts of ClNO_2 on air

pollution in the PRD region.

Table 6. The summary of the impacts of CINO₂ on the next-day enhancement of ozone and radical production is based on a box model that is constrained by field observations in previous literature.

Location	Duration	CINO ₂	Daytime average	Daytime average	References
		Maximum (ppb)	Enhancement P(O ₃)	Enhancement P(RO _x)	
Heshan, China	2019. 11	1.5	1.0%-4.9%	<2.2%	this work
Shanghai, China	2020.10-11	0.4	-	<1.0%	Lou et al., 2022
Wangdu, China	2014.6-7	2.1	3%	<10%	Tham et al., 2016
Seoul, Korea	2016.5-6	2.5	1.0-2.0%	-	Jeong et al., 2019
Hongkong, China	2013.11-12	4.7	11.0-41.0% ^a	-	Wang et al., 2016
California, US	2010.5-6	1.5	15.0% ^b	17%	Riedel et al., 2014
Wangdu/Beijing/ Mt. Tai, China	2017-2018	1.7	1.3%-6.2%	1.3%-3.8%	Xia et al., 2021

^a used a box model to estimate the following evolution after the plume passing measurement site and the impacts on the next-day air quality; ^b not constrained the observed CINO₂ concentration but simulated the observed maximum CINO₂ case to predict the corresponding upper contribution.

2. The authors are suggested to distinguish the concepts of “chlorine” and “chloride”. In many places of this paper, “chlorine” should be used instead of “chloride”. Examples include but are not limited to lines 38 and 39.

Thanks for the correction and we revised it accordingly.

3. Please carefully check the language. Below are two examples: 1. Line 113, change “ubiquity” to “ubiquitous”; 2. Line 122: change “both they” to “they both”.

We polished the language throughout the manuscript accordingly.

4. Some doubts about the CIMS measurement. (1) Was any background measurement performed during the campaign? If yes, please present the result. If no, please clarify this point and remind readers about the uncertainty caused.

Yes, backgrounds were detected for N₂O₅ and CINO₂ during the campaign and the results are shown in Figure. S1, for example. The green squares and line represent the average values of background and background interpolation, respectively. Which confirmed the low background of CIMS in measuring N₂O₅ and CINO₂ in the ambient condition. In the revised manuscript, we added a brief description of the background measurement.

Line 618.

A1. The measurement background and calibration of CIMS

The background measurement of CINO₂ and N₂O₅ was performed during the campaign. Figure 1A showed an example of the background check at the beginning of the campaign, which confirmed the negligible background signal in the measurement of CINO₂ and N₂O₅ in the ambient condition.

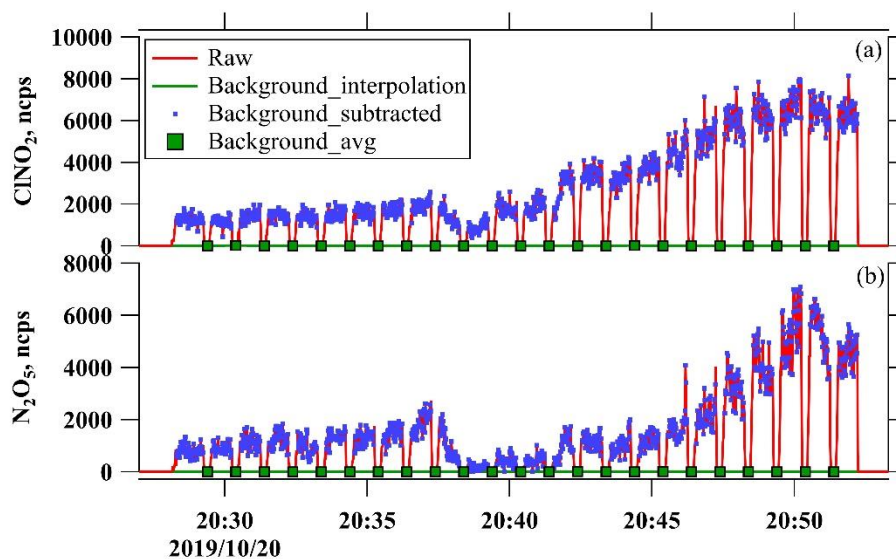


Figure S1. Background deduction for N_2O_5 (a) and ClNO_2 (b) (take October 20, 20:28-20:52 pm as an example)

(2) How often was the calibration for N_2O_5 and ClNO_2 ? Regular checking of the sensitivity of N_2O_5 or ClNO_2 is critical to ensure the reliable quantification of CIMS measurement. In case regular calibration is challenging in the field, the authors may investigate the record of instrument voltages, pressure, and other parameters to show how stable was the instrument during the campaign.

We appreciate the reviewer for the valuable suggestions. We do not often do N_2O_5 or ClNO_2 calibration during the campaign. Indeed, regular checking of the sensitivity is critical and it is also challenging to calibrate in the field. After inspection, the main parameters (pressure: voltages, etc.) of the CIMS were relatively stable, indicating that the CIMS is operating stably during the campaign. In addition, the comparison with the state of the instrument when N_2O_5 and ClNO_2 were calibrated in the laboratory showed no significant difference. Therefore, the concentration data of N_2O_5 and ClNO_2 are reliable.

Line 642. In this study, the sensitivity of the instrument was calibrated after the campaign. The main parameters (pressure: voltages, etc.) of the CIMS were checked every day and were relatively stable, indicating that the CIMS is operating stably during the campaign.

(3) How much is the inlet artifact? As we know, N_2O_5 may deposit on the inlet wall and produce ClNO_2 .

We agree that N_2O_5 deposition on the inlet wall may produce ClNO_2 in the field measurement. In this campaign, a total flow rate of 8 slpm in sample mode ensured that residence time in the inlet was minimal to reduce the conversion of N_2O_5 to ClNO_2 . Furthermore, throughout the campaign, there were periods when N_2O_5 is high up to 800 pptv while ClNO_2 is below 30 pptv (Figure S2), which indicates that the conversion of N_2O_5 to ClNO_2 on the inlet walls is controllable when considering the overall measurement uncertainty (Bannan et al., 2015).

Ref:

Bannan, T. J., et al. (2015), *The first UK measurements of nitryl chloride using a chemical ionization mass spectrometer in central London in the summer of 2012, and an investigation of the role of Cl atom oxidation*, *J. Geophys. Res. Atmos.*, 120, 5638–5657, doi:10.1002/2014JD022629

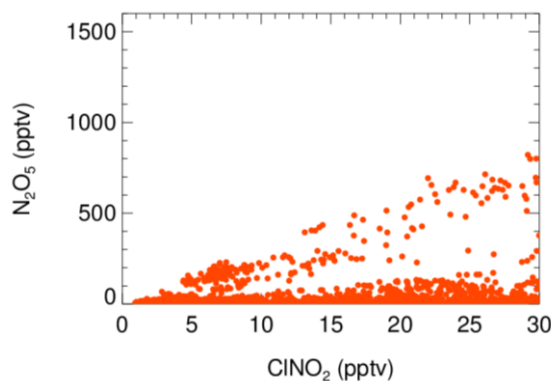


Figure S2. The N_2O_5 level when ClNO_2 is lower than 30 ppt.

Minor comments:

1. Line 227-231: it is more relevant to discuss nocturnal PNO_3 , as N_2O_5 and ClNO_2 are mostly produced during the night.

Here we did not delete the statement about the daily average level of PNO_3 since we believe this parameter is valuable for intercomparison for the following related research. And we added the discussion about the nocturnal PNO_3 as follows.

Line 236. At night, the nitrate radical production rate was $1.8 \pm 1.5 \text{ ppbv h}^{-1}$ on campaign average (median, 1.4 ppbv h^{-1}).

2. Line 398: change “ NO_2 ” to “ NO_2^+ ”.

Corrected accordingly.

3. Line 437-438: In my opinion, when ClNO_2 shows no correlation with PNO_3 , no clear conclusion can be drawn. For example, highly variable ClNO_2 yield may also cause poor ClNO_2 - PNO_3 correlation.

Yes, this is attributed to ClNO_2 formation affected by many reaction steps including NO_3 reacts with other reactants as well as N_2O_5 uptake and ClNO_2 yield. We admit the conclusion that ClNO_2 formation is not limited by NO_3 production is a little bit arbitrary. Therefore, we changed the statement as follows. We also deleted the statement in the abstract correspondingly.

Line 451. In addition, the variation of N_2O_5 uptake coefficient and ClNO_2 yield also results in the weak correlation between NO_3 production rate and ClNO_2 concentration. The weak correlation reflects the highly variable chemical processes from NO_3 production to ClNO_2 production in this region.

4. Line 498: In figure 9, it shows that $\text{O}_3 + \text{OVOC}$ pathway has the largest contribution to $\text{P}(\text{ROx})$. This is somehow surprising to me. Please double check this result.

This is a very interesting question. We noticed it mainly attributed to the reaction of $\text{O}_3 + \text{DCB}$ (unsaturated dicarbony) and $\text{O}_3 + \text{EPX}$ (epoxide). The DCB and EPX were mainly produced from XYO and XYP (dominated by m_p_Xylene and o_Xylene), these two species were 3.55 and 1.25 ppbv on average and much higher than

previous observations in Heshan in 2014 (1.62 and 0.58 ppbv, Yang et al., ACP, 2017) and Wangdu, 2014 (0.15 and 0.11 ppbv, Tan et al., ACP, 2017). This result indicates that the role of these aromatic hydrocarbons had a large ozone potential by producing considerable OVOCs.

And we checked our model setting and input and confirmed no mistake or error in the model.

Ref:

Yang, Y. D., Shao, M., Kessel, S., Li, Y., Lu, K. D., Lu, S. H., Williams, J., Zhang, Y. H., Zeng, L. M., Noelscher, A. C., Wu, Y. S., Wang, X. M., and Zheng, J. Y.: How the OH reactivity affects the ozone production efficiency: case studies in Beijing and Heshan, China, Atmos. Chem. Phys., 17, 7127-7142, 10.5194/acp-17-7127-2017, 2017.

Tan, Z., Fuchs, H., Lu, K., Hofzumahaus, A., Bohn, B., Broch, S., Dong, H., Gomm, S., Haeseler, R., He, L., Holland, F., Li, X., Liu, Y., Lu, S., Rohrer, F., Shao, M., Wang, B., Wang, M., Wu, Y., Zeng, L., Zhang, Y., Wahner, A., and Zhang, Y.: Radical chemistry at a rural site (Wangdu) in the North China Plain: observation and model calculations of OH, HO₂ and RO₂ radicals, Atmos. Chem. Phys., 17, 663-690, 10.5194/acp-17-663-2017, 2017.

5. Line 528: Again, it is surprising to me that Cl radical only have 3% to 4% contribution to long-chain alkane oxidation during morning hours. Please double check this result.

Thanks for the reviewer's kind reminder, the time series of modeled Cl radical shows that the mean diurnal peak is 2.1×10^3 molecules cm^{-3} . And the modeled OH radical had the mean diurnal peak of 3.9×10^6 molecules cm^{-3} , which is at the moderate level of the reported observations. The above two aspects resulted in the small contribution of Cl radical to the long-chain alkane oxidation contributions (we double-checked the reaction rate constant and the calculation code). We also compared the modeled Cl and OH with the result reported in Weybourne, the UK by Bannan et al., JGR, (2017), they modeled a case with the mean diurnal peak of Cl and OH of 1.6×10^3 molecules cm^{-3} and 5.6×10^6 molecules cm^{-3} , and the average fraction of alkane oxidation contributed by Cl is <1%, which also consistent with that reported in London (Bannan et al., JGR, 2015). This intercomparison provides confirmation of the plausibility of our results.

We noticed that the C₁₂-C₁₄ data measured by PTR-MS was only valid from 16th Oct. to 17th Nov. 2019, therefore we updated the calculation and revised the manuscript as follows.

Line 563. We observe small contributions of chlorine radical with a percentage of 4.3%, 4.3% and 3.8% for n-decane, n-dodecane, and n-tetradecane, respectively, during the period (Oct. 16th to Nov. 17th, 2019) when the long-chain alkanes measurement was valid. We also checked the role of chlorine radicals in short-chain alkanes oxidation, obtaining a slightly larger contribution than the long-chain alkanes, which is attributed to a relatively larger reaction rate constants between Cl with OH with respect to the short-chain alkanes. The daytime average contributions of Cl ranged from 1.4% - 1.6% varied by the chain length of the alkanes. Therefore, we concluded that chlorine radicals liberated by ClNO₂ photolysis play a role in the oxidation of alkanes in the morning time, but are not critical compared with OH oxidation on the daytime average. We note that several studies reported other sources produced a large number of halogen radicals like Cl₂ (Liu et al., 2017; Xia et al., 2020), BrCl (Peng et al., 2021), the daytime reaction of HCl with OH (Riedel et al., 2012; Eger et al., 2019; Li et al., 2019). These may cause more alkanes oxidized by halogen radicals. However, it is not possible to assess the overall impacts by constraining all precursors of chlorine radical in this work, which may warrant further investigation by more

comprehensive field studies equipped with the instruments for detecting these species.

Ref.

Bannan, T. J., Booth, A. M., Bacak, A., Muller, J. B. A., Leather, K. E., Le Breton, M., Jones, B., Young, D., Coe, H., Allan, J., Visser, S., Slowik, J. G., Furger, M., Prevot, A. S. H., Lee, J., Dunmore, R. E., Hopkins, J. R., Hamilton, J. F., Lewis, A. C., Whalley, L. K., Sharp, T., Stone, D., Heard, D. E., Fleming, Z. L., Leigh, R., Shallcross, D. E., and Percival, C. J.: The first UK measurements of nitryl chloride using a chemical ionization mass spectrometer in central London in the summer of 2012, and an investigation of the role of Cl atom oxidation, *Journal of Geophysical Research-Atmospheres*, 120, 5638-5657, 10.1002/2014jd022629, 2015.

Bannan, T. J., Bacak, A., Le Breton, M., Flynn, M., Ouyang, B., McLeod, M., Jones, R., Malkin, T. L., Whalley, L. K., Heard, D. E., Bandy, B., Khan, M. A. H., Shallcross, D. E., and Percival, C. J.: Ground and Airborne UK Measurements of Nitryl Chloride: An Investigation of the Role of Cl Atom Oxidation at Weybourne Atmospheric Observatory, *Journal of Geophysical Research-Atmospheres*, 122, 11154-11165, 10.1002/2017jd026624, 2017.

6. Line 533-538: Did any signals of Cl₂, BrCl, Br₂ detected during the campaign? Recent studies found that these more reactive halogens may have larger impacts than ClNO₂.

This is a very interesting topic and we did not notice these species before. We have not calibrated m/z 196.8 (Cl₂), m/z 240.8 (BrCl) and m/z 284.7 (Br₂) in the laboratory and field. In this study, we used a semi-quantitative method to infer the sensitivity of these species, which is divided into two steps: 1) obtain the dissociation voltage of the I-cluster and establish a functional relationship between the dissociation voltage and the relative sensitivity (Lopez-Hilfiker et al., 2016); 2) establish the relative transmission efficiency curve of the CIMS through laboratory experiments in order to correct the mass discrimination effect (Heinritzi et al., 2016). In this way, we get the concentrations of Cl₂, BrCl and Br₂ as shown in Figure S3. We agree with the reviewer's opinion that other sources of halogen may have an important impact on some VOCs species. However, the mean concentration of Cl₂ in Heshan was only 2.0±3.7 ppt during the campaign, and the average mixing ratios of BrCl and Br₂ were less than 1.0 ppt. Since we focus on the topic on ClNO₂ chemistry and did not well calibrate the measurement sensitivity of Cl₂, BrCl, Br₂, thus we did not add the content in the revised manuscript.

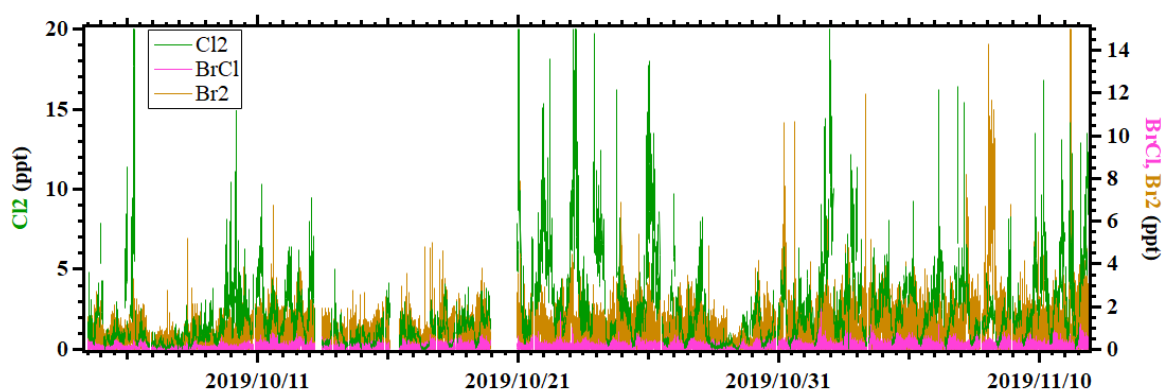


Figure S3. Time series of Cl₂, BrCl and Br₂.

Ref:

Lopez-Hilfiker, F. D., et al., (2016), Constraining the sensitivity of iodide adduct chemical ionization mass spectrometry to multifunctional organic molecules using the collision limit and thermodynamic stability of iodide ion adducts, Atmos. Meas. Tech., 9, 1505–1512, doi:10.5194/amt-9-1505-2016.

Heinritzi, M., et al., (2016), Characterization of the mass-dependent transmission efficiency of a CIMS, Atmos. Meas. Tech., 9(4), 1449–1460, doi:10.5194/amt-9-1449-2016.

7. As mentioned above, the conclusion part can be more concise.

We shortened the conclusion part accordingly; More details can be found in our revised manuscript.