

Winter observations of ClNO₂ in northern China: Spatiotemporal variability and insights into daytime peaks

Men Xia¹, Xiang Peng¹, Weihao Wang^{1,8}, Chuan Yu^{1,2}, Zhe Wang⁶, Yee Jun Tham^{7,3}, Jianmin Chen⁴, Hui Chen⁴, Yujing Mu⁵, Chenglong Zhang⁵, Pengfei Liu⁵, Likun Xue^{2,4}, Xinfeng Wang², Jian Gao³, Hong Li³, and Tao Wang¹

General Comments:

This paper compares the formation of ClNO₂ and its impact on the tropospheric radical budget at 3 ground sites in China during winter and summer over an extended measurement period. It is important in that it shows in places subject to fresh emissions of NO, that ClNO₂ formation can be even more important in the summer and during the daytime when compared to its formation during the winter in the same places.

The body of the paper details that (1) less photochemical production of O₃, (2) more fresh NO emissions at the Wangdu & Beijing sites in winter and (3) especially dry conditions at the Beijing site in winter are responsible for suppressing the NO₃ radical production // dominating the loss of NO₃ & therefore suppressing ClNO₂ production in winter when compared to summer. This, in addition to seasonal differences in their calculated uptake coefficients of N₂O₅ and yields of ClNO₂ ultimately explain the lower concentrations of ClNO₂ during winter compared to summer at the sites. The observations and analysis presented highlight that ClNO₂ can be important during summer and during the day, and that the behavior of observed ClNO₂ is explainable by our understanding of its chemistry under different conditions (e.g. more NO, less O₃, low RH). My biggest concern with the paper in its current form is that the abstract and conclusion focus largely on the fact that “observed ClNO₂ is higher in summer than winter at these sites” and the underlying messages of “why this occurs is in line with the current understanding of the formation of ClNO₂” and “the summer/winter trends at these ground sites which experience a lot of fresh pollution are not generally representative of trends we expect in the residual boundary layer where ClNO₂ formation is higher” may be lost on the casual reader. I would like to see the abstract and conclusions revised to better communicate that portion of the results (which is well communicated in the body of the text).

Overall, the methods and assumptions are well outlined, the discussion is detailed, the results are presented in a logical structure, the language is clear (easy to read- well done!), and their conclusions are well reasoned. The analysis within represents a clear step forward in our understanding of the formation and role of ClNO₂ in the troposphere under different conditions. There are a few important citations missing from the paper, that I believe should be added, and I have suggested several modifications to figures that could improve the overall communication of the results. Ultimately, I recommend that this paper be accepted with minor revisions.

Specific Comments:

Title: It's probably worth mentioning the summer /winter comparison which makes this work novel or the control of the NO emissions in the title. Maybe "Local seasonal emissions control ClNO₂ formation in northern China: Spatiotemporal variability and insights in into daytime peaks" or "Comparing the sensitivity of winter and summer ClNO₂ formation in Northern China to local emissions: Spatiotemporal variability and insights in into daytime peaks"?

Line 57-59: I suggest adding a sentence about the impact of Cl radicals in the non-polluted troposphere (since that is much of their impact on a global scale). This will set up your readers to better interpret the differences you see between sites since they experience more fresh pollution than studies in other regions.

Line 70-71: I would also cite Simpson et al., 2015 (ACS: Tropospheric Halogen Chemistry: Sources, Cycling, and Impacts <https://pubs.acs.org/doi/10.1021/cr5006638>) either here or somewhere else in the introduction.

Line 98-101: This statement is not an accurate summation of the reference since they conclude that Cl is the dominant radical source in the polluted MBL there (at least in the early morning). I would suggest revising it to: "The role of ClNO₂ in the radical budget could be more important than that of OH in winter, because OH production is reduced in winter owing to lower concentrations of O₃ and H₂O vapor in this season. Haskins et al., 2019 recently confirmed that, even when compared to OH, Cl atoms from ClNO₂ photolysis can be the dominant early morning radical source and the dominant integrated daily radical source over the polluted marine boundary layer downwind of the northeast US."

Lines 109-119: I would also mention longer NO_x lifetimes allows NO_x to spread further distances from its local sources during winter. You may also clarify that the variability in seasonal Cl availability you reference is unique to the NCP.

Line 118-119: This line is quite a strong statement. I suggest reframing it, particularly since the sites examined in this work are subject to quite substantial changes in the precursor conditions. (e.g. "Because of the competing trends and variability in chemical precursors to N₂O₅ and ClNO₂, it is not clear whether ClNO₂ formation is always more prevalent during winter compared to summer, particularly in regions that experience large variability in the conditions of the advected air masses they experience.")

At some point in the introduction, there needs to be some discussion about our understanding of ClNO₂ formation in regions subject to fresh pollution (e.g. lots of fresh NO) verses in aged polluted air masses verses in clean air. All the results in the paper can be explained with what we already know about ClNO₂ formation in different types of air masses- but you need to set the reader up for what to expect in each different type of air mass before you get to the results. I think it will set up the discussions of why the trends at the Wangdu site look as they do in a way that will be useful to readers less familiar with the formation process of ClNO₂.

Table 1: I think the "Site Categories" are misleading/unclear. The discussion of each site is excellent & builds a great picture of the conditions experienced, but this table does not summarize those well. On line 158-159 you state that the Wangdu site experiences heavy pollution from coal burning and road traffic. In the results section (lines 285-288) you state that both the Wangdu and Beijing sites experience

high NO_x and low O₃. However, Wangdu is categorized as a “rural” site, while Beijing is categorized as an “urban” site. While the Wangdu site is certainly more remote than the upwind Beijing site, the category of “rural” is typically used to describe low CO/NO_x conditions and urban used to describe places with more CO/ NO_x. I suggest either recategorizing Wangdu as “remote polluted” and Beijing as “upwind urban polluted” or adding a column to the table with the average daily NO_x and O₃ concentrations observed in each observation period. I think the latter might be more useful (because then you could tell that the sites experience rather different pollution conditions in the different seasons). Finally categorizing Mt. Tai as a “mountain” site seems redundant and non-descriptive- perhaps a “remote residual layer” site or “remote clean” site. The abstract and conclusion where these categorical descriptors are used should also be updated (lines 25, 541)

Lines 224-244: A citation for the rate constants used in the box model for each of these equations is needed for reproducibility.

Line 230-257: Some discussion about $k(\text{NO}_3)$ is needed. What VOCs were used? If you did not measure the full suite of VOCs then you would underestimate $k(\text{NO}_3)$ in Eq. 2 thereby impacting the calculated uptake of N₂O₅ and yield of ClNO₂. A statement about the uncertainty arising from this is needed at minimum.

Figure 1: This figure could be improved by making the various y-axis limits consistent across all sites when possible. I see no reason why the jNO₂ axis can't be consistent across all panels with a max value at 8×10^{-3} (as it is on later figures). I would also label the site not with just their name but their “category” e.g. Wangdu: remote polluted). If visibility of the data is impacted, I suggest highlighting the axis differences at minimum.

Figure 2: Again, this figure could be improved if the y-axis limits were consistent when possible, allowing for easier comparisons. I also think it would be interesting to see the winter and summer data on the same plot rather than split up as it is. Perhaps by using color to denote winter verses summer rather than chemical species/ axis and a translucent shading.

Lines 310-350: There is a really important discussion here about the role that shifting NO concentrations plays in driving the difference in the winter and summer measurements at Wangdu and Beijing. However, this important information is not currently communicated in any of the figures of the paper, but easily could be given the observations made.

(This may be beyond the scope of the authors at this state in revision... But I think it would be interesting to see how ClNO₂ formation compared in the winter vs summer observations but grouped by daily peak NO (or NO_x) concentrations or daily averaged NO (or NO_x) conditions during the day and during the nighttime. (e.g. a bar chart showing ClNO₂ concentrations on the y axis, grouped by NO concentrations on the x axis with a bar for winter right next to a bar for summer in each of the NO groupings along the x axis. If the winter/summer average diurnal profiles were combined on Figure 2 in to only 3 panels, you could then show such a figure in panel d, e, & f for each site. It would show how the distribution of NO_x as NO vs. NO₂ changed between seasons, as well as likely organize why you see more ClNO₂ when there is less NO, but more NO₂... If that didn't organize well, even showing ClNO₂ concentrations grouped by the calculated rate of production of NO₃ would communicate the main message of the paper while explaining the average diurnal profiles in a visual way.)

Figure 3: This would be a great summary figure to have in the literature. However, there appear to be several missing measurements of ClNO₂/N₂O₅, particularly those over the US. The ones off the top of my head which are missing are as follows, but I would encourage the authors to ensure they have included all measurements to date, as I expect there at least a few other observations that are missing...

Faxon et al., 2015: <https://www.mdpi.com/2073-4433/6/10/1487>

Haskins et al., (2018): <https://agupubs.onlinelibrary.wiley.com/doi/full/10.1029/2018JD028786>

McDuffie et al., 2019: <https://acp.copernicus.org/articles/19/9287/2019/>

Jeong et al., (2019) : <https://acp.copernicus.org/articles/19/12779/2019/>

Line 401-408: These are potentially the most important results of the paper and I'd like to see the few sentences describing them be communicated more clearly. E.g. Explicitly explain why k₁ is lower (wintertime temperatures, etc). Explicitly explain why you have lower [NO₂] * [O₃] in winter (e.g. less photochemical production of O₃, more NO in winter titrating available O₃, despite longer NO₂ lifetimes in winter). Also while you give avg NO_x conditions of the sites during winter there is no discussion about what those are during summer at these sites. Adding that info to Table 1 as previously suggested and perhaps in the paragraphs where the site results are individually introduced would set this discussion up better.

Figure 4: Similar to my comments about Figure 2, I wonder if it would be useful to also show on panel A, not just the mean in the winter verses in the summer, but also with the winter and summer measurements at each site separated into two different NO_x (or NO) regimes (e.g. fresh pollution present verses not? Also, on panel B would it be possible to show the fraction of loss from NO verses VOCs with hatching? In the text it should also be stated that the loss to VOCs is potentially underestimated (See prior comments).

Lines 439-449: You do not mention if you looked at how IH₂O⁻ was changing during these daytime peaks? I suspect its not a problem given the infield calibrations, but it is worth adding a sentence to mention you'd check that as well.

Figure 7: Why is HCHO photolysis not included? I expect it to be a large contributor to the radical budget in at least some of these sites in these periods... Additionally, there's evidence that the presence of Cl radicals oxidizing VOCs enhances the production of HCHO and therefore OH concentrations so the differences between the with and without ClNO₂ cases would be underestimated without considering the contributions from HCHO as well? At least some discussion is needed as to why HCHO is not considered part of the radical budget of OH.

Lines 514 –522: I'd like to see these results compared to results from other papers that have done this sort of analysis (e.g. Riedel et al., 2012, Young et al., 2014, Haskins et al., 2019, etc.). The conditions of the sites analyzed in this work are sufficiently different from other in the literature (e.g. more fresh NO more coal burning, more aerosol SA, way more HONO) that contrasting your results to those paper's results provides novel insights into the variability of ClNO₂ production/ importance to the radical budget during winter in different chemical regimes. Also, Young et al., 2014 (<https://acp.copernicus.org/articles/14/3427/2014/>) is relevant to this work & I'd suggest adding it as a citation.

Lines 529-531: This is the only time that the measurements presented in this paper are put into context into how much they matter in the context of the globe. I'd like to see this sentiment present in the conclusions/ abstract as well to contextualize the results. I suggest adding a statement like this to the conclusions between lines 546-547.

Lines 541: Again, I don't think its appropriate to categorize the sites as "rural" given their polluted conditions (change to "remote polluted"). Update this line to reflect changes in its "categorization" in Table 1 and in the Abstract.

Technical Corrections

Line 84: Bertram et al., 2009 should be cited as Bertram & Thornton 2009 as it only has 2 authors.

Line 103: This reference should be a citation to Haskins et al., 2018 (Wintertime Gas-Particle Partitioning and Speciation of Inorganic Chlorine in the Lower Troposphere Over the Northeast United States and Coastal Ocean <https://agupubs.onlinelibrary.wiley.com/doi/full/10.1029/2018JD028786>) rather than Haskins et al., 2019 (Anthropogenic control over wintertime oxidation of atmospheric pollutants <https://agupubs.onlinelibrary.wiley.com/doi/10.1029/2019GL085498>)

Line 142: "mostly during the *heading* period" should likely be "mostly during the *heating* period" ...