

Anonymous Referee #3

We thank the referee for the comments and suggestions which help us improve the quality of the paper. We have made all of the suggested changed and/or clarifications.

This paper describes measurements of nitryl chloride and associated species at a site in the North China Plain (NCP), and presents model estimates of the impact of this active chlorine compound on ozone formation in that environment. The measurements are very interesting and the associated analysis makes some important points about ClNO₂ in the residual boundary layer of the polluted NCP. The presentation of the work is quite well done, it is concise and well organized and the important aspects are well explained. There are only a few issues for the authors to address to make this paper acceptable for publication.

General Comments

In general the English in the paper is quite good, however there are a number of instances disagreements between the noun and the verb (e.g. singular when it should be plural, etc.). The authors briefly mention measurements of gas-phase HCl, but since this is an important fraction of the chloride available for activation, it deserves more details. Also, the morning time source of Cl atoms will have a corresponding source of HCl, as most Cl + VOC reactions produce HCl.

Response: Thanks for the comments and suggestions. The English have been edited.

We agree that the gas-phase HCl can be an important fraction of the chloride aerosol available for activation. This information has been added into the text (section 3.5) to support the chloride availability.

The presence of gas-phase HCl (mean of 0.78 ppbv) during the night also can continuously replenish the Cl⁻ aerosol.

As for the Cl source, our model analysis had been constrained by the HCl measurement and the mean concentration of HCl was shown in the supplement information (Table S2) to indicate the level of HCl at Wangdu. The contribution of HCl to the daily Cl radical production is much smaller than the photolysis of ClNO₂, especially in the morning time (Figure 10a). The related sentence has been revised to include this information.

It shows that photolysis of ClNO₂ was the predominant source of Cl in Wangdu compared to the reaction of HCl and OH and photolysis of Cl₂.

Specific Comments:

1. Page 2, Line 31: While ClNO₂ is not as well studied as N₂O₅, there are loss mechanisms for ClNO₂ at night. Kim et al., [2014] show that ClNO₂ can be deposited on water surfaces. Roberts et al., [2008] showed that ClNO₂ can be taken up on low pH surfaces (and will make Cl₂). It is fair to say that because of its low aqueous solubility [Sander, 2015], ClNO₂ losses are likely much slower than N₂O₅, and to a first approximation can probably be neglected.

Response: Yes, it is possible for the ClNO₂ to undergo loss mechanism under certain conditions. Therefore, we have rephrased the sentence into:

ClNO₂ may subject to some loss processes on water and other surfaces (e.g. Roberts et al., 2008; Kim et al., 2014), but the night-time losses of ClNO₂ are expected to be negligible due to its low solubility (Sander, 2015).

2. Page 4., Lines 8&9. When you say “tropospheric ozone” that implies a broad scale, really you are talking about ozone in the Beijing urban area.

Response: Thanks for the suggestion. The word tropospheric has been omitted.

3. Page 5, Line 12. Did you see any evidence of Cl₂, at the mass of the cluster ion I(Cl₂)⁻ ?

Response: We did not measure the cluster ion of I(Cl₂)⁻ in our CIMS setup.

4. Page 7, Line 28, “constrained into” is the wrong expression, a model can be ‘constrained by’ observations.

Response: We thank the reviewer for identifying this error. The phrase has been revised in the text.

5. Page 14, Line 29, “less’ should be ‘lesser’.

Response: Corrected.

6. Figure 2. The yellow color is hard to see.

Response: The color in Figure 2 has been changed.

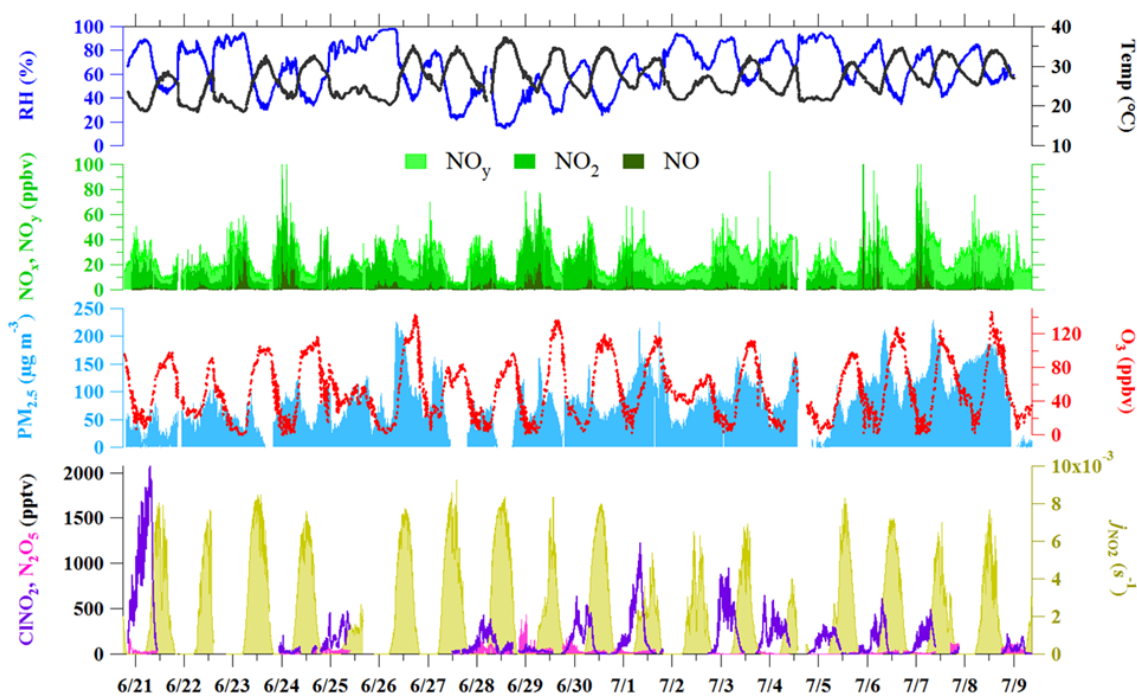


Figure 2

References

Kim, M. J., Farmer, D. K., and Bertram, T. H.: A controlling role for the air–sea interface in the chemical processing of reactive nitrogen in the coastal marine boundary layer, *Proc. Natl. Acad. Sci.*, 10.1073/pnas.1318694111, 2014.

Roberts, J. M., Osthoff, H. D., Brown, S. S., and Ravishankara, A. R.: N₂O₅ oxidizes chloride to Cl₂ in acidic atmospheric aerosol, *Science*, 321, 1059., 2008.

Sander, R.: Compilation of Henry's law constants (version 4.0) for water as solvent, *Atmos. Chem. Phys.*, 15, 4399-4981, 10.5194/acp-15-4399-2015, 2015.