

## Anonymous Referee #1

We thank the referee for the comments and suggestions. Our response and the corresponding changes are listed below (in blue wording).

Tham et al. present a comprehensive set of measurements and analysis focusing on ClNO<sub>2</sub> formation at a ground site in Northern China. I thought this was a well written manuscript which should be published after my suggestions below have been considered.

Minor issues.

1. pg 2 line 12. (R5) please use the proper chemical symbol for a reversible reaction (the symbol used denotes resonance)

**Response:** The symbol " $\leftrightarrow$ " in R5 has been changed to " $\rightleftharpoons$ " to represent reversible reaction.

2. pg 5 - section 2.2. What were the response factors for N<sub>2</sub>O<sub>5</sub> and ClNO<sub>2</sub> at m/z 235 and 208 when the Corona discharge and the <sup>210</sup>Po were used?

It may be worthwhile to add more detail about the calibration here, and add a figure of an example calibration sequence to the supplemental. The Wang et al. (2016) describes results from a different study, where there was a CRDS N<sub>2</sub>O<sub>5</sub> instrument.

**Response:** The average response factor of  $1.11 \pm 0.23$  pptv/Hz for 235 m/z (N<sub>2</sub>O<sub>5</sub>) and  $1.10 \pm 0.11$  ppt/Hz for 208 m/z (ClNO<sub>2</sub>) when the corona discharge was used, while the average response factor was  $1.32 \pm 0.35$  pptv/Hz for 235 m/z and  $1.40 \pm 0.28$  pptv/Hz for 208 m/z were determined when the radioactive source was used. This information has been added into the main text. An additional figure has been added into the supplemental to show the example of calibration for N<sub>2</sub>O<sub>5</sub> and ClNO<sub>2</sub> when using the corona discharge and the <sup>210</sup>Po (Figure S3).

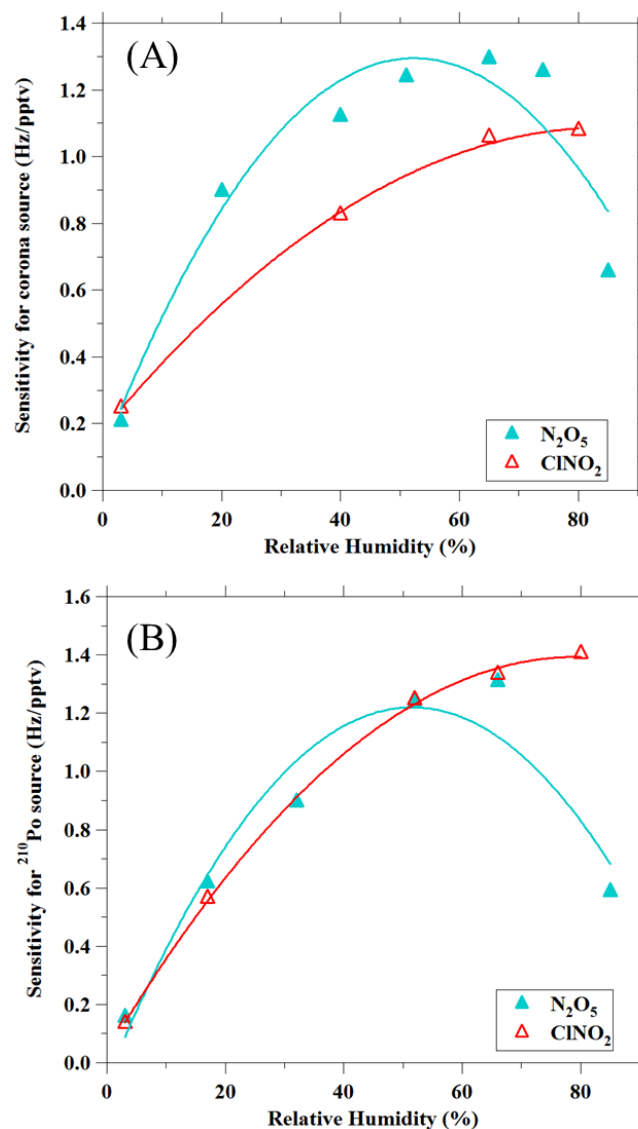


Figure S3. An example of sensitivity for  $\text{N}_2\text{O}_5$  and  $\text{ClNO}_2$  against the relative humidity when (a) corona discharge and (b)  $^{210}\text{Po}$  were used. The solid line represents the curve fits of the data.

Was the humidity in the CIMS inlet controlled?

The humidity in the CIMS inlet was not controlled. As mentioned in the text, we did standard addition of  $\text{N}_2\text{O}_5$  through the inlet every 3 hours to monitor the sensitivity change of  $\text{N}_2\text{O}_5$  due to ambient changes (i.e. RH and aerosol loading).

I am concerned about the measurement of  $\text{N}_2\text{O}_5$  using  $m/z$  235. Can you comment on potential interferences arising from clustering of iodide with organic acids?

There is little information in the literature on the potential interference of  $235 m/z$  regarding the clustering of iodide with organic acids/organics. According to a personal discussion with Y. Chao (from University of Helsinki), in their laboratory measurement with iodide time of flight (ToF)-CIMS, one of the organo-nitrate peaks ( $\text{C}_8\text{H}_{13}\text{O}_7\text{N}$ ) indeed located within  $235 m/z$ . The ambient concentration of this species should be at sub-ppt level, so we believe that our  $235$

$m/z$  signal should be due to  $N_2O_5$  and not largely affected by the organic molecules. In addition, the organo-nitrates is expected to peak in the daytime due to photochemistry, but the 235  $m/z$  did not show significant signals in the midday or late afternoon (as shown by the diurnal pattern in Figure 4 in the text).

Is  $m/z$  210 consistent with the relative isotopic abundance of  $^{37}Cl$ ?

The 208  $m/z$  and 210  $m/z$  are consistent with the relative isotopic abundance of chlorine. Plot of 208  $m/z$  and 210  $m/z$  yields a slope of 0.31 which is near the theoretical value of isotopic chlorine of 0.32. This additional information has been added into the main text and supplement.

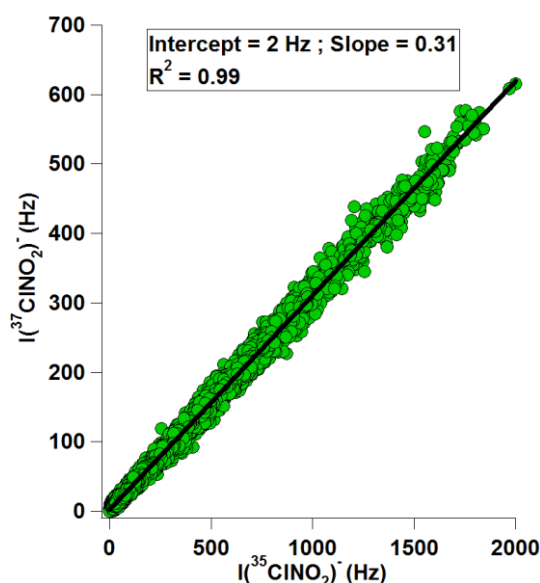


Figure S4. Scatter plot of 210  $m/z$  against the 208  $m/z$ .

3. pg 7, line 30 - the  $CINO_2$  cross-sections were remeasured in 2008 by Ghosh et al. (JPC A 116, 6003 (2012)). Please indicate which cross-sections were used in this work.

**Response:** The cross-sections used in the photolysis frequency of  $CINO_2$  for the current analysis was based on the recommendation of Jet Propulsion Laboratory (JPL; Sander et al., 2006). This information has been added into the main text.

Reference:

Sander, S. P., Friedl, R., Golden, D., Kurylo, M., Moortgat, G., Wine, P., Ravishankara, A., Kolb, C., Molina, M., and Finlayson-Pitts, B.: Chemical kinetics and photochemical data for use in atmospheric studies evaluation number 15, JPL Publication 06-2, 2006.

4. pg 9 line 29. The homogeneous hydrolysis rate by Wahner et al. is likely incorrect (see, e.g., Brown et al., Science, 2006). Consider omitting it.

**Response:** Thanks for the suggestion. We have omitted the homogeneous hydrolysis rate in the analysis.

5. pg 11 line 15. His last name is spelled Riedel.

**Response:** We have corrected the typo.

6. pg 12, equation (6). There may also be "loss" of CINO<sub>2</sub> due to entrainment upwards from the residual layer (not just downward mixing). Hence, the levels in the residual layer could be higher than calculated here.

**Response:**

Good point. We agree with the reviewer that there could be upward diffusion of CINO<sub>2</sub> from the residual layer (RL). But the possibility of the upward diffusion is much less than that of the downward diffusion, considering that the mixing between PBL and free troposphere (i.e. the upward diffusion from RL to free troposphere) is much less efficient than the mixing within the PBL (i.e. the downward diffusion from RL to surface). Therefore, in our study, we only considered the downward diffusion of CINO<sub>2</sub> from the RL to the surface to estimate the CINO<sub>2</sub> concentration in RL, and the estimated value is subject to slight underestimation.

We have added a sentence into the main text:

*‘The estimated CINO<sub>2</sub> concentration in RL may subject to underestimation due to the omission of the upward diffusion of CINO<sub>2</sub> in RL to the free troposphere.’*

7. pg 12 line 19 "This result suggest that elevated CINO<sub>2</sub> may always present in the residual layer of this region." One cannot logically conclude from some observations to "always" as there may be the odd exception. Suggest rephrasing to "frequently" or similar.

**Response:** The word ‘always’ was rephrased to ‘frequently’.

8. pg 15 line 27- many references are incomplete (missing doi, volumes, page numbers, etc.).

**Response:** All of the references have been revised.

9. pg 22 (Table 1). Please state the uncertainties for each of the measurements.

**Response:** The uncertainty of each measurement have been added to the Table 1.

10. General. There are a few minor grammatical errors scattered throughout the document. I would suggest asking a native English speaker to read through the manuscript a couple of times and make corrections where warranted.

**Response:** Thanks for the suggestion. The grammatical errors in the manuscript have been corrected.