Anonymous Referee #2

We thank the reviewers for their attention to this manuscript. We have made nearly all of the suggested changed and/or clarifications. Our response is in blue wording.

Summary: Tham et al. present a novel set of measurements of ClNO2, N2O5, alongside supporting observations of select trace gases and aerosol. The observations provide new insight on under sampled regions of the atmosphere, particularly with respect to molecules that are recently emerging as being important for atmospheric oxidation.

The analysis follows prior work in this area conducted in the US and Europe and is well founded in the observations. I have a few select comments that should be addressed prior to publication. There are also a series of grammatical errors that should be addressed before the paper makes its way to publication in ACP.

Specific Comments:

1. Page 3 lines 1-5: Perhaps discuss in terms of the ClNO2 photolysis lifetime instead of concentrations following sunrise.
Response:
Thanks for pointing out. The sentence was rephrased to show the lifetime of $ClNO_2$ due to photolysis after sunrise.

2. Page 5 line 10: The use of I- ion chemistry in extremely polluted regions such as this is limited and it is perhaps likely that other atmospheric compounds contribute to the observed signals at 235 and 208 m/z. A few quality control questions: 1) What is the 208/210 ratio for ClNO2 detection, is this consistent with the natural abundance of Cl isotopes? and 2) is there any signal intensity during the daytime (midday / late afternoon) at 235 and 208/210 m/z that would indicate a contribution from other molecules at these masses?
Response: The ratio of 208 *m/z* and 210 *m/z* (from the plot below) yields a slope of 0.31 which is consistent with the theoretical value of isotopic chlorine of 0.32. This additional information has been added into the main text and supplement (Figure S4).

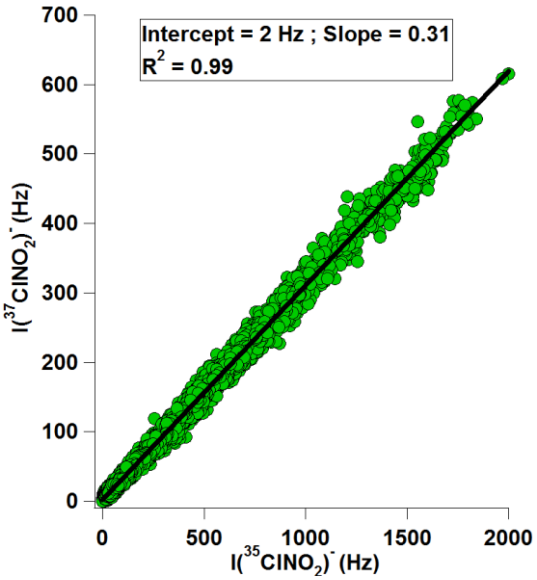

Figure S4. Scatter plot of 210 *m/z* against the 208 *m/z*.

No significant signal intensity was observed in the midday or late afternoon as shown in the diurnal pattern of N_2O_5 and $ClNO_2$ in Figure 4 of the main text.

3. Page 7 line 31: What is meant by the "physical loss rate of the unmeasured species was set as the 6 h lifetime for the mixing height of 1000 m." Is deposition included in these models?
Response: Yes, deposition was included in the MCM model. This is an item for the non-chemical loss of species either through deposition or mixing in the model. The phrase means a lifetime with respect to a physical first order loss of 6 h which equals to a deposition velocity of V_d = 4.63 cm s^{-1} in a 1000 m deep boundary layer.

In order to be more specific, we have rephrased the sentence in the text to:
The lifetime of the unmeasured species with respect to physical first order loss rate was set as 6 h which equals to a deposition velocity of 4.63 cm s^{-1} in a 1000 m deep boundary layer.

4. Page 10 line 6: Converting the computed lifetimes to reactive uptake coefficients based on measured Sa would be a helpful addition as the community is well calibrated to that language. It would also be helpful to include specific values for the ClNO2 yields that best fit the observations.
Response: We agree with the reviewer. Specific values for the reactive uptake coefficients and $ClNO_2$ yields have been added into the main text as following:

... This gives larger N_2O_5 uptake coefficient (γ) of 0.030 in the megacity case compared to 0.014 in the campaign average (estimated from equation 3, where c_{N2O5} is the mean molecular speed of N_2O_5).

$$k(N_2O_5)_{het} = \frac{1}{4} c_{N2O5} S_a \gamma \qquad \textit{(Eq 3)}$$

... The $ClNO_2$ yield that best fit the observations can be estimated by dividing the $ClNO_2$ concentration over the integrated amount of N_2O_5 uptake loss, as shown in equation (4).

$$\phi = \frac{[ClNO_2]}{\int k(N_2O_5)_{het}[N_2O_5]\,dt} \qquad \textit{(Eq 4)}$$

Comparable average $ClNO_2$ yield of 0.30 and 0.35 are found in the campaign average and megacity case, respectively.

5. Page 11 line 10: What is the accuracy in the measured surface area? Is the surface area reported here dry or wet? If you need a factor of three change in gamma(N2O5) to match the data, is that within the uncertainty in Sa? Especially given that a growth factor may be needed to convert the measured dry to the relevant ambient Sa.
Response: We need to clarify that the S_a reported in this manuscript is for the ambient condition, not in the dry state. The wet diameter of particles was calculated with kappa-Köhler function based on the measured size-resolved kappa (refer to the main text). We have made slight modification to the wording of the sentence in the main text to make it clearer.

The uncertainty derived from the estimation of size-resolved kappa was estimated at 16% which is consistent with the uncertainties reported for growth factor and kappa (<20%) (e.g. Yeung et al., 2014; Liu et al., 2014; Hennig et al., 2005). So we do not think that the uncertainty of the calculated S_a may contribute to a factor of 2.4 change in the N_2O_5 uptake.

Reference:

Yeung, M. C., Lee, B. P., Li, Y. J., and Chan, C. K.: Simultaneous HTDMA and HR-ToF-AMS measurements at the HKUST Supersite in Hong Kong in 2011, J. Geophys. Res.-Atmos., 119, 9864-9883, 10.1002/2013JD021146, 2014.

Hennig, T., Massling, A., Brechtel, F. J., and Wiedensohler, A.: A tandem DMA for highly temperature-stabilized hygroscopic particle growth measurements between 90% and 98% relative humidity, J. Aerosol Sci., 36, 1210-1223, 10.1016/j.jaerosci.2005.01.005, 2005.

Liu, H. J., Zhao, C. S., Nekat, B., Ma, N., Wiedensohler, A., van Pinxteren, D., Spindler, G., Muller, K., and Herrmann, H.: Aerosol hygroscopicity derived from size-segregated chemical composition and its parameterization in the North China Plain, Atmos. Chem. Phys., 14, 2525-2539, 10.5194/acp-14-2525-2014, 2014.

6. Page 12 line 15: The calculation of RL ClNO2 is very sensitive to the boundary layer height at 5 and 8AM. Are there measurements of this height? Also, what is the accuracy in the WRF calculated nocturnal boundary layer height? It is hard to imagine this is accurate to the values quoted here (50 and 72m).

Response: We agree that the calculated $ClNO_2$ concentration in the residual layer depends on the boundary layer (BL) heights used in the study. We used very high spatial resolution (1 km), high temporal resolution (1h) and observational-nudging techniques in the WRF simulation, which shall give more reliable information than the common global operational analysis data which typically has a spatial resolution of 0.5-1 degree (~50 to 100 km) and temporal resolution of 3-6 h. Previous studies have shown that the parameterization option used in our study (the Yonsei University scheme) appeared to generally reproduce the PBL features in various regions. For instance, Hu et al. (2010) compared observed PBL heights at 8 stations in US and simulated ones from WRF using YSU scheme, and found that the relative simulation bias to be about -13% during the early morning (calculated based on the Fig. 7 in Hu et al., 2010). The information on the bias from the previous study has been added into the text.

We want to clarify that the goal here is not simulate the $ClNO_2$ in the residual layer but rather to estimate its rough concentration levels. We recalculated the $ClNO_2$ concentration with different height of boundary layer. Increasing the simulated nocturnal boundary layer height (5AM) by a factor of 2 while remaining the same boundary layer height at 8AM causes a difference of less than 10% in the $ClNO_2$ concentration. A similar result is obtained while doubling the boundary layer height at 8AM and keeping the simulated nocturnal boundary layer height at 5AM. We have added this result in the revision.

Reference:

Hu, X. M., Nielsen-Gammon, J. W., and Zhang, F. Q.: Evaluation of three planetary boundary layer schemes in the WRF Model, J. Appl. Meteorol. Clim., 49, 1831-1844, 10.1175/2010JAMC2432.1, 2010.