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 ClNO2 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 "↔" in R5 has been changed to "⇌" to represent reversible reaction.

2. pg 5 - section 2.2. What were the response factors for N2O5 and ClNO2 at m/z 235 and 208 when the Corona discharge and the 210Po 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 N2O5 instrument.

Response: The average response factor of 1.11±0.23 pptv/Hz for 235 *m/z* (N_2O_5) and 1.10±0.11 ppt/Hz for 208 *m/z* ($ClNO_2$) when the corona discharge was used, while the average response factor was 1.32±0.35 pptv/Hz for 235 *m/z* and 1.40±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_2O_5 and $ClNO_2$ when using the corona discharge and the ^{210}Po (Figure S3).

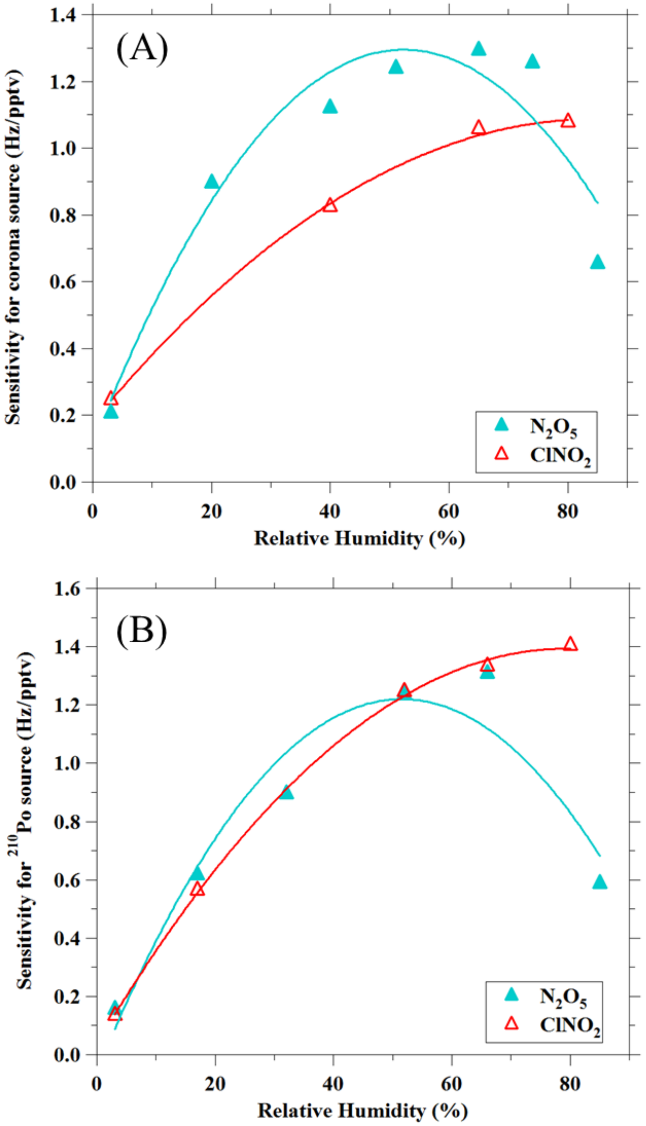

Figure S3. An example of sensitivity for N_2O_5 and $ClNO_2$ against the relative humidity when (a) corona discharge and (b) ^{210}Po were used. The solid line represents the curve fits of the data.

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 N_2O_5 through the inlet every 3 hours to monitor the sensitivity change of N_2O_5 due to ambient changes (i.e. RH and aerosol loading).

I am concerned about the measurement of N2O5 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 ($C_8H_{13}O_7N$) 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 37Cl?

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.

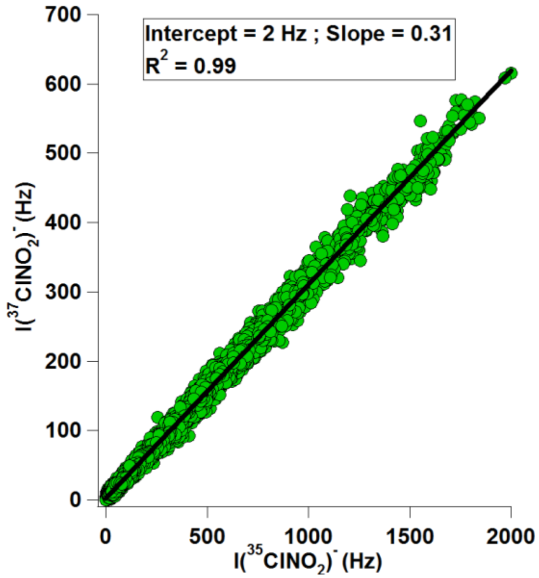

Figure S4. Scatter plot of 210 *m/z* against the 208 *m/z*.

3. pg 7, line 30 - the $ClNO_2$ 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 $ClNO_2$ for the current analysis was based on the recommendation of Jet Propulsion Laboratory (JPL; Sander et al., 2011). It should be noted that the j_{ClNO2} would be around 20% smaller using the most recent NASA-JPL recommendation based on a work by Ghosh et al. (2012).These information have been added into the main text.

Reference:

Ghosh, B., Papanastasiou, D. K., Talukdar, R. K., Roberts, J. M., and Burkholder, J. B.: Nitryl chloride ($ClNO_2$): UV/vis absorption spectrum between 210 and 296 K and O(^{3}P) quantum yield at 193 and 248 nm, J. Phys. Chem. A, 116, 5796-5805, 10.1021/jp207389y, 2012.

Sander, S. P., Abbatt, J., Barker, J. R., Burkholder, J. B., Friedl, R. R., Golden, D. M., Huie, R. E., Kolb, C. E., Kurylo, M. J., Moortgat, G. K., Orkin V. L., and Wine, P. H.: Chemical kinetics and photochemical data for use in atmospheric studies, Evaluation No. 17, JPL Publication 10-6, Jet Propulsion Laboratory, Pasadena, 2011 (http://jpldataeval.jpl.nasa.gov).

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 ClNO2 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 $ClNO_2$ 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 $ClNO_2$ from the RL to the surface to estimate the $ClNO_2$ concentration in RL, and the estimated value is subject to slight underestimation.

We have added a sentence into the main text:

'*The estimated $ClNO_2$ concentration in RL may subject to underestimation due to the omission of the upward diffusion of $ClNO_2$ in RL to the free troposphere.*'

7. pg 12 line 19 "This result suggest that elevated ClNO2 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.

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).

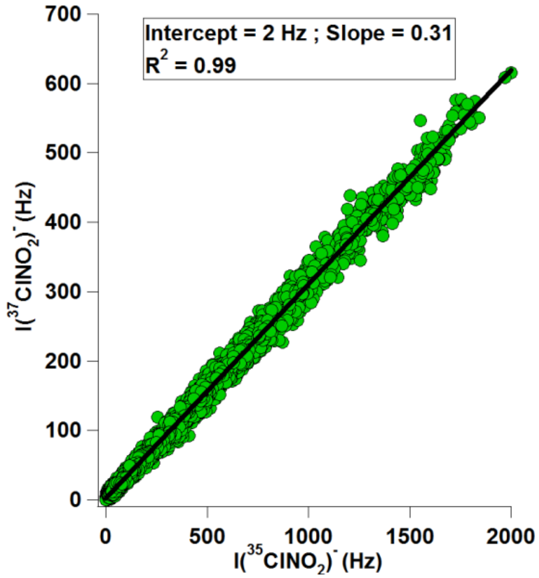

Figure S4. Scatter plot of 210 *m/z* against the 208 *m/z*.

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*).*

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

… 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.

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 during the night (mean = 0.78 ppbv) 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 $ClNO_2$, especially in the morning time (Figure 10a). The related sentence has been revised to include this information.

It shows that photolysis of $ClNO_2$ *was the predominant source of Cl in Wangdu compared to the reaction of HCl and OH and photolysis of* Cl_2*.*

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 $ClNO_2$ to undergo loss mechanism under certain conditions. Therefore, we have rephrased the sentence into:

$ClNO_2$ 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 $ClNO_2$ 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 $I(Cl_2)^-$ 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.

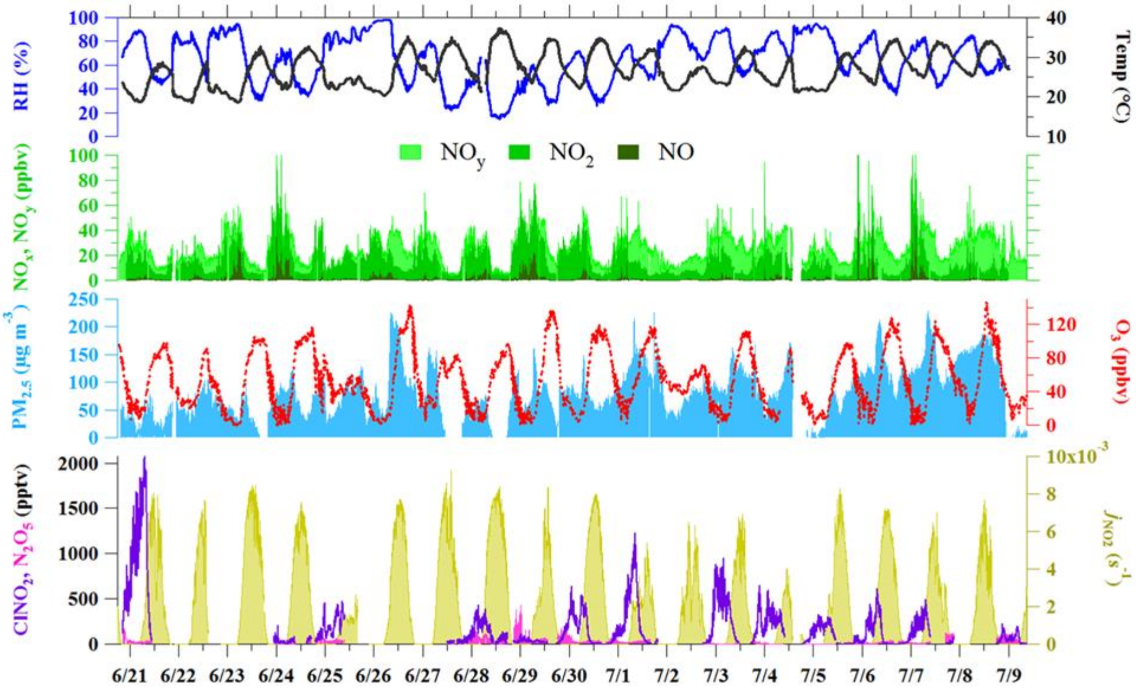

Figure 2

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.

Significant concentrations of nitryl chloride sustained in the morning: Investigations of the causes and impacts on ozone production in a polluted region of northern China

Yee Jun Tham[1], Zhe Wang[1], Qinyi Li[1], Hui Yun[1], Weihao Wang[1], Xinfeng Wang[2], Likun Xue[2], Keding Lu[3], Nan Ma[4], Birger Bohn[5], Xin Li[5], Simonas Kecorius[4] and Johannes Größ[4], Min Shao[3], Alfred Wiedensohler[4], Yuanhang Zhang[3], and Tao Wang[1*].

[1]Department of Civil and Environmental Engineering, The Hong Kong Polytechnic University, Hong Kong, China,
[2]Environment Research Institute, Shandong University, Jinan, Shandong, China,
[3]State Key Joint Laboratory of Environmental Simulation and Pollution Control, College of Environmental Sciences and Engineering, Peking University, Beijing, China,
[4]Leibniz Institute for Tropospheric Research, Permoserstr. 15, 04318 Leipzig, Germany,
[5]Forschungszentrum Jülich, Institut IEK-8: Troposphäre, 52425 Jülich, Germany.

[*]*Correspondence to:* T. Wang (cetwang@polyu.edu.hk)

Abstract. Nitryl chloride ($ClNO_2$) is a dominant source of chlorine radical in polluted environment and can significantly affect the atmospheric oxidative chemistry. However, the abundance of $ClNO_2$ and its exact role are not fully understood under different environmental conditions. During the summer of 2014, we deployed a chemical ionization mass spectrometer to measure $ClNO_2$ and dinitrogen pentoxide (N_2O_5) at a rural site in the polluted North China Plain. Elevated mixing ratios of $ClNO_2$ (>350 pptv) were observed at most of the nights with low levels of N_2O_5 (<200 pptv). The highest $ClNO_2$ mixing ratio of 2070 pptv (1-min average) was observed in a plume from megacity (Tianjin) and was characterized with faster N_2O_5 heterogeneous loss rate and $ClNO_2$ production rate compared to average condition. The abundant $ClNO_2$ concentration kept increasing even after sunrise and reached a peak 4 hours later. Such highly sustained $ClNO_2$ peaks after sunrise are discrepant from the previously observed typical diurnal pattern. Meteorological and chemical analysis show that the sustained $ClNO_2$ morning peaks are caused by significant $ClNO_2$ production in the residual layer at night followed by downward mixing after break-up of the nocturnal inversion layer in the morning. We estimated that ~1.7-4.0 ppbv of $ClNO_2$ would exist in the residual layer in order to maintain the observed morning $ClNO_2$ peaks at the surface site. Observation-based box model analysis show that photolysis of $ClNO_2$ produced chlorine radical with a rate up to 1.12 ppbv h^{-1}, accounting for 10-30% of primary RO_x production in the morning hours. The perturbation in total radical production leads to an increase of integrated daytime net ozone production by 3% (4.3 ppbv) on average, and with a larger increase of 13% (11 ppbv) in megacity outflow that was characterized with higher $ClNO_2$ and relatively lower OVOC to NMHC ratio.

1 Introduction

Nitryl chloride ($ClNO_2$) is a nocturnal reservoir of reactive nitrogen and chlorine radicals (Cl) that play crucial roles in the next day photochemistry (Young et al., 2012; Mielke et al., 2013; Sarwar et al., 2014). Formation of $ClNO_2$ begins with the oxidation of nitrogen dioxide (NO_2) by ozone (O_3) to yield nitrate radical (NO_3) (R1). NO_3 is very susceptible to sunlight and can react rapidly with nitrogen oxide (NO) and volatile organic compounds (VOCs) (R2-4). At nightfall, the NO_3 begins to accumulate and can further react with NO_2 to give N_2O_5 (R5).

$$NO_2 + O_3 \rightarrow NO_3 \qquad \text{(R1)}$$

$$NO_3 + h\nu \rightarrow 0.9NO_2 + 0.9O + 0.1NO + 0.1O_2 \qquad \text{(R2)}$$

$$NO_3 + NO \rightarrow 2NO_2 \qquad \text{(R3)}$$

$$NO_3 + VOC \rightarrow \text{products} \qquad \text{(R4)}$$

$$NO_3 + NO_2 + M \leftrightharpoons \cancel{\leftrightarrow} N_2O_5 + M \qquad \text{(R5)}$$

N_2O_5 exist in thermal equilibrium with NO_2 and NO_3, and heterogeneously reacts with chloride containing aerosols (Cl^-) to form $ClNO_2$ and nitrates (NO_3^-) (R6), or undergoes hydrolysis to produce water-soluble nitric acids (HNO_3) (R7) (Finlayson-Pitts et al., 1989).

$$N_2O_5 + Cl^- (aq) \rightarrow ClNO_2 + NO_3^- (aq) \qquad \text{(R6)}$$

$$N_2O_5 + H_2O (l) \rightarrow 2HNO_3 \qquad \text{(R7)}$$

The abundance of $ClNO_2$ produced from the heterogeneous uptake of N_2O_5 depends on the availability of Cl^- aerosols and nitrogen oxides ($NO_x = NO + NO_2$) in the atmosphere (Bertram and Thornton, 2009; Brown and Stutz, 2012). Efficient production of $ClNO_2$ was found in the polluted coastal regions that are directly impacted by abundant ~~of~~ sea salt aerosol and urban emissions. For instance, Osthoff et al. (2008) measured more than 1 ppbv of $ClNO_2$ in the urban outflows along the coast of Texas; high $ClNO_2$ mixing ratios of up to 3.6 ppbv were detected in the polluted Los Angeles basin (Riedel et al., 2012; Wagner et al., 2012; Mielke et al., 2013). Significant production of $ClNO_2$ was not previously expected in inland regions with limited Cl^- sources until Thornton et al. (2010) found $ClNO_2$ mixing ratio of up to 0.45 ppbv in urban plumes ~~of~~ from Boulder, Colorado. ~~They~~ This observation suggested ~~implied~~ the presence of ~~abundant~~ non-oceanic chloride from coal-fired power plants, industries, biomass burning, road salts and soil-dust in inland regions which could support widespread production of $ClNO_2$. Since then, other studies have observed $ClNO_2$ mixing ratios, ranging from tenths of pptv ~~up~~ to 1.3 ppbv in polluted inland regions (Mielke et al., 2011; Phillips et al., 2012; Riedel et al., 2013; Faxon et al., 2015).

~~$ClNO_2$ is unreactive during the night as it has negligible nocturnal loss processes.~~ $ClNO_2$ 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 $ClNO_2$ are expected to be negligible due to its low solubility (Sander, 2015). Its primary sink is via photolysis during the day, yielding a highly reactive chlorine radical and NO_2 (R8).

$$ClNO_2 + h\nu \rightarrow Cl + NO_2 \qquad (R8)$$

Therefore, $ClNO_2$ typically shows a ~~clear~~ distinct diurnal pattern where it accumulates ~~primarily~~ at night and decreases gradually to very low ~~concentrations~~ levels in the daytime. Under conditions of reduced photolysis, small $ClNO_2$ concentrations may persist during the daytime. For example, Mielke et al., (2013) found that the median lifetime of $ClNO_2$ in respect to photolysis could reach 1.2 h ~~mixing ratios of $ClNO_2$ could reach 100 pptv~~ even 4 hours after sunrise at Pasadena (with mixing ratios of $ClNO_2$ of 100 pptv), which was partly caused by the heavy cloud and aerosol cover or fog at the site. More recent measurements ~~on~~ at surface sites ~~at~~ in London and ~~Texas~~ Houston observed cases with $ClNO_2$ increase ~~of $ClNO_2$ soon~~ after sunrise and peak several hours later with concentration of 40-150 pptv (photolysis lifetime of 2.8-3.5 h) that could result from transport processes of $ClNO_2$ from region with higher $ClNO_2$ concentrations (Bannan et al., 2015; Faxon et al., 2015).

Photolysis of nighttime accumulated $ClNO_2$ during daytime was found to cause rapid production of Cl, with ~~peak of~~ production rate up to 0.03 - 0.50 ppbv h^{-1} (Osthoff et al., 2008; Thornton et al., 2010; Phillips et al., 2012; Riedel et al., 2012, Riedel et al., 2014; Mielke et al., 2015). This Cl precursor was shown to be an important primary radical source as it constituted ~9-13% of the daily primary radical production~~s~~ (Edwards et al., 2013; Young et al., 2014) and exceeded the production of hydroxyl radical (OH) via photolysis of O_3 by up to a factor of 10 for several hours after sunrise (Phillips et al., 2012). Subsequently, the released Cl would oxidize VOCs and enhance ozone production in polluted regions through reactions of R9-R15.

$$Cl + RH \rightarrow R + HCl \qquad (R9)$$

$$R + O_2 + M \rightarrow RO_2 + M \qquad (R10)$$

$$RO_2 + NO \rightarrow RO + NO_2 \qquad (R11)$$

$$RO + O_2 \rightarrow OVOC + HO_2 \qquad (R12)$$

$$HO_2 + NO \rightarrow OH + NO_2 \qquad (R13)$$

$$NO_2 + h\nu \rightarrow NO + O(^3P) \qquad (R14)$$

$$O(^3P) + O_2 + M \rightarrow O_3 + M \qquad (R15)$$

For example, Osthoff et al. (2008) reported an increase of 6 and 9 ppbv of ozone in Houston by constraining 0.65 and 1.5 ppbv of $ClNO_2$ into their model, respectively. Neglecting the contribution of HONO, 1.5 ppbv of $ClNO_2$ could increase ~12 ppbv of ozone in Los Angeles (Riedel et al., 2014). Chemical transport model simulations by Sarwar et al. (2014) suggested that high $ClNO_2$ concentrations in ~~region like~~ China and Western Europe can lead to daily 8-hour average ozone increase of up to 7 ppbv.

Despite the important role in photochemistry, studies on this Cl precursor in China are sparse. Most of the previously reported studies of $ClNO_2$ were conducted in the US (e.g. Osthoff et al., 2008; Thornton et al., 2010; Riedel et al., 2012; Riedel et al., 2013; Mielke et al., 2013; Faxon et al., 2015), Canada (Mielke et al. 2011, 2015), with a few in Europe (Phillips et al., 2012; Bannan et al., 2015). Recently, measurements of $ClNO_2$ were conducted in Hong Kong,~~ of~~ southern China~~ have~~, which observed high levels of $ClNO_2$ at both surface and mountain sites (Tham et al., 2014; X. Wang et al., 2014; Wang et al., 2016). In a well-processed regional plume, maximum $ClNO_2$ of 4.7 ppbv and N_2O_5 of up to 7.7 ppbv were observed at Mt Tai Mao Shan (957 m a.s.l.), and box model calculations showed significant impacts of the $ClNO_2$ on the next day ozone production, with an increase of ozone of up to 41% (Wang et al., 2016).

The North China Plain (NCP) covers an area of 409,500 km^2 and is home to megacities like Beijing, Tianjin, and Shijiazhuang. It is one of the most polluted regions in China according to the Ministry of Environmental Protection (MEP China, 2015). Due to intense and fast economic development, the emission of NO_x has increased steadily, reaching a peak of 127 Gg N yr^{-1} in 2011 (Mijling et al., 2013). High ~~levels~~ concentrations of ground-level O_3 were frequently reported in the NCP. For instance, a maximum hourly value of up to 286 ppbv was observed in a rural site north of Beijing (Wang et al., 2006). ~~Tropospheric ozone~~Ozone over the last two decades has increased at a rate of 2-5% yr^{-1} (Ding et al., 2008; Zhang et al., 2014). The abundant NO_x and O_3 coupled with the large loading of chloride-containing aerosol (Sun et al., 2006; Huang et al., 2014; Sun et al., 2015) may make the heterogeneous uptake and chlorine activation processes particularly important in driving the formation of ozone and secondary aerosol in this region.

In summer 2014, we deployed a chemical ionization mass spectrometer (CIMS) for the first field measurement of $ClNO_2$ in the NCP. It was a part of an international collaborative field campaign, the CARE-Beijing 2014 (Campaigns of Air Quality Research in Beijing and Surrounding Regions) with the major aim to understand the oxidative processes in the region. In the present paper, we give an overview of the measurement results of $ClNO_2$ and its precursors, N_2O_5, and related species. We then examine the factors that affect the $ClNO_2$ production. We also investigate the cause of sustained $ClNO_2$ peaks observed after sunrise and the potential sources of aerosol chloride that drive the $ClNO_2$ productions. The impacts of the $ClNO_2$ on the primary radical productions and ozone formation are then assessed with a measurement-constraint chemical model.

2 Methodology

2.1 Site description

This study took place at a semi-rural site (38.665° N, 115.204° E) in Wangdu County of Hebei province. Figure 1 shows the location of the measurement site in relation to the topography and emission sources in the NCP. Although the site is located in an area with rural/suburban development, it is impacted by anthropogenic emissions. The national capital, Beijing (population > 21 million), is located ~170 km in the northeast, and another megacity, Tianjin (population >15 million) is situated about 180 km to the east, while Shijiazhuang (population >12 million) which is the capital and largest city of Hebei province ~~(population >12 million)~~ is 90 km to the southwest. In addition to these megacities, a prefecture-level city~~ with population of ~11 million~~, Baoding, is 33 km to the northeast (Fig. 1b). The immediate surrounding area (i.e. within 5 km) of the sampling site is mostly covered by agricultural lands (Fig. 1c). The closest large local emission sources include a national highway and a provincial road, which are about 1-2 km away from the site. The major town area of Wangdu County is located ~5 km to the northwest while many densely spaced villages are sporadically spread around the area.

Dozens of coal-fired power stations are situated within a radius of 200 km. Among the nearest are Datang power station (capacity 650 MW) which is 27 km in the northeast and Dingzhou power station (capacity 2520 MW) which is 35 km in the southwest. Emission from the agriculture activities also have impacts on the site. The field study is in the harvesting season of winter wheat (Sun et al., 2007) and burning activities were frequently observed in the region, as indicated by the active fire hotspots obtained from FIRMS (MODIS C5, data available at https://earthdata.nasa.gov/firms) (see Fig. S1 in supplementary information (SI)). The less developed area of Taihang Mountains range (main peak = 2,882 m a.s.l) is located at 50-100 km in the north to west sector and the nearest coastline of Bohai Sea is ~200 km in the east.

2.2 Chemical ionization mass spectrometer

$ClNO_2$ and N_2O_5 were concurrently measured with a quadrupole chemical ionization mass spectrometer (THS Instruments, Atlanta). The principle and the calibration of the CIMS have been described in Wang et al. (2016). Briefly, iodide ions (I^-) were used as primary ions and the N_2O_5 and $ClNO_2$ were detected as ion clusters of $I(N_2O_5)^-$ and $I(ClNO_2)^-$ at 235 and 208 *m/z*, respectively. The CIMS measured N_2O_5 and $ClNO_2$ with a time resolution of ~7s. Data were later converted into 1 min averages for further analysis. During the Wangdu field study, the instrument background was determined by diverting the sampling flow through a filter fully-packed with activated carbons. Off-line calibrations of N_2O_5 and $ClNO_2$ were performed every day on the site, while standard addition of N_2O_5 into the ambient air was performed every 3 hours to monitor the sensitivity changes due to ambient conditions. More details on the calibration procedures can be found elsewhere (Wang et al., 2016). A corona discharge device (THS Instruments) was applied to generate I^- from mixture of CH_3I/N_2 (0.3% v/v) at the beginning of the measurement period (20 June – 26 June 2014) due to delay in shipment of a radioactive source. The large background signals from the corona discharge source (see Fig. S2) gave rise to detection limit of 16 pptv for N_2O_5 and 14 pptv for $ClNO_2$ (3σ, 1 min-averaged data). The corona discharge source was replaced by an alpha radioactive source, ^{210}Po (NRD, P-2031-2000) from 27 June 2014 until the end of the~~ measurements~~study, which improved the~~. The~~ detection limits for the latter period were improved to 7 pptv for N_2O_5 and 6 pptv for $ClNO_2$ (3σ, 1 min-averaged data). The average sensitivity of the system with corona discharge setup was 1.11±0.23 pptv/Hz for N_2O_5 and 1.10±0.11 pptv/Hz for $ClNO_2$, with the average sensitivity of 1.32±0.35 pptv/Hz and 1.40±0.28 pptv/Hz for N_2O_5 and $ClNO_2$, respectively, for radioactive source (see Fig. S3).

The CIMS instrument was housed in a trailer. The sampling line was a 7.5-m long PFA-Teflon tubing (¼” O.D.). The inlet was set at ~2 m above the roof and ~10 m from ground level with a total sampling flow of ~11 standard liters per minute (SLPM). The inlet configuration was similar to a virtual impactor which is intended to remove large particles (e.g. Kercher et al., 2009; Kulkarni et al., 2011). Only ~4 SLPM from the total flow was diverted to the CIMS, ozone and NO_x analyzer while the rest was dumped. The total residence time in the sampling system was less than a second. In order to minimize the effect of the particles deposited on the surface of the sampling inlet, the orifice, tubing and fittings were replaced and washed with ultrasonic every day (Wang et al., 2016). Examination of the measurement data did not show evidence of conversion of ambient N_2O_5 to $ClNO_2$ in the inlet. For instance, there were occasions when the N_2O_5 signal increased significantly with no enhancement in $ClNO_2$, suggesting that the $ClNO_2$ was not produced in the inlet. Measurement of 208 *m/z* and its isotopic ($I(^{37}ClNO_2)^-$) was consistent with the natural abundance of chlorine isotopes (refer Fig. S4). The uncertainty of the measurement is estimated to be ±25% with a precision of 3%. The ambient measurements of N_2O_5 and $ClNO_2$ were available from 20 June to 9 July 2014.

2.3 Other measurements

The measurement techniques for trace gases and aerosols which are used to support the present analysis are summarized in Table 1. During the Wangdu study, most of the trace gases were simultaneously measured by different instruments/techniques. The agreement between these instruments/techniques and justification on the data set selections are discussed in another manuscript (Z. Tan et al., 2016, submitted to this issue of Atmospheric Chemistry and Physics). ~~Basically~~Briefly, NO and NO_2 were measured by the chemiluminescence/photolytical conversion techniques, while total reactive nitrogen (NO_y) was determined by the chemiluminescence method with a molybdenum oxide (MoO) catalytic converter. O_3 was quantified by a UV absorption analyzer. Sulfur dioxide (SO_2) was measured by a pulsed UV fluorescence analyzer and carbon monoxide (CO) with an infrared photometer. C_2-C_{10} hydrocarbons (NMHCs), formaldehyde (HCHO), and other oxygenated hydrocarbons (OVOCs) were measured with an online gas chromatograph (GC) equipped with a mass spectrometer and a flame ionization detector (FID), a Hantzsch fluorimetric monitor, and proton-transfer-reaction mass spectrometer (PTR-MS), respectively (Yuan et al., 2010, 2012; M. Wang et al., 2014). Methane was measured by cavity ring down spectroscopy technique (CRDs). Measurement of nitrous acid (HONO) was performed by a long-path absorption photometer (LOPAP) instrument (X. Li et al., 2014; Liu et al., 2016).

Particle mass concentrations ($PM_{2.5}$) were measured using a standard Tapered Element Oscillating Microbalances (TEOM). The ionic compositions of $PM_{2.5}$ were determined by a gas aerosol collector (GAC)-ion chromatography system (Dong et al., 2012). The dry-state particle number size distribution was determined by combining the data (Pfeifer et al., 2014) from a Mobility Particle Size Spectrometer (Dual TROPOS-type SMPS; Birmili et al., 1999; Wiedensohler et al., 2012) and an Aerodynamic Particle Size Spectrometer (TSI-type APS model 3321; Pfeifer et al., 2016) covering the size ranges from 4-800 nm (mobility particle diameter) and 0.8-10 µm (aerodynamic particle diameter), respectively. The ambient (wet) particle number size distributions as function of the relative humidity were calculated from a size-resolved kappa-Köhler function determined from real time measurement of a High Humidity Tandem Differential Mobility Analyzer (HHTDMA) (Hennig et al., 2005; Liu et al., 2014). Ambient particle surface area concentrations (S_a) were calculated based on the (wet) ambient particle number size distribution assuming spherical particles.

Meteorological parameters including wind direction, wind speed, relative humidity (RH), pressure and temperature were measured with an ultrasonic anemometer and a weather station on a 20-m height tower which was situated 30 m from the trailers. Photolysis frequencies were determined from actinic flux densities measured by a spectroradiometer (Meteorologie Consult) (Bohn et al., 2008).

2.4 Meteorological and dispersion models

Weather Research and Forecasting model (WRF) was used for the simulation of meteorological fields during the study. Four nested domains were adopted for WRF simulations, covering whole China, northern China, North China Plain, and the surrounding area of the Wangdu site, with a grid size of 27, 9, 3 and 1 km, respectively. Other settings utilized in this study were the same as those described in Wang et al. (2016). The simulation results from the WRF were validated by using hourly surface observation data obtained from China Meteorological Agency (CMA). WRF simulations generally reproduced the meteorology conditions in NCP during the campaign (refer to Table S1).

With the hourly WRF output, HYbrid Single-Particle Lagrangian Integrated Trajectory model (HYSPLIT) (Draxler et al., 2014) was adopted to investigate the history of air masses that arrived at the measurement site. The HYSPLIT model was run in the dispersion mode for 12 hours backward in time, where 2500 particles were released at the sampling site and the hourly positions of these particles were tracked during this period. More detailed settings and descriptions of the HYSPLIT model can be found in Wang et al. (2016).

2.5 Chemical box model

In order to evaluate the contributions of $ClNO_2$ to daytime primary radical and O_3 production, an explicit observation-based chemical box model was utilized. The model was developed based on the latest version of Master Chemical Mechanism v3.3 (Jenkin et al., 2015) and was updated with a Cl chemistry module including 205 reactions of the inorganic mechanisms of Cl and VOCs degradations initiated by Cl (Xue et al, 2015).

The observation data of $ClNO_2$, HCl, HONO, O_3, NO, NO_2, SO_2, CO, CH_4, C_2-C_{10} NMHCs, OVOCs (methanol, formaldehyde, acetone, acetaldehyde, acetic acid, MEK, MTBE), H_2O, temperature, pressure and aerosol surface area were averaged or interpolated. ~~and then~~ The model was constrained ~~into~~ by the observation data ~~the model~~ every 10 min. The average concentration for each species and meteorological input are shown in Table S2. The photolysis frequency input of NO_2 (j_{NO2}), HONO (j_{HONO}), O_3 (j_{O1D}) and $ClNO_2$ (j_{ClNO2}) were determined from the field measurement. The j_{ClNO2} here was determined based on the cross section recommended by Sander et al. (2011). It should be noted that the j_{ClNO2} would be around 20% smaller using the most recent NASA-JPL recommendation based on a work by Ghosh et al. (2012). ~~while photolysis~~ Photolysis frequency of other related compounds were predicted following the function of solar zenith angle (Saunders et al., 2003) in the model and were scaled according to the field measured j_{NO2}. ~~The physical loss rate of the unmeasured species was set as the 6 h lifetime for the mixing height of 1000 m~~. 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. The model was run for 24-hours period with the starting time set at 00:00 local time and was repeatedly run for 6 times to stabilize the unmeasured intermediate species. The daytime output from the final run was used for further analysis of the primary radical production and O_3 production and loss processes.

3 Results and discussion

3.1 Overview of measurement results

Figure 2 depicts the temporal variations of $ClNO_2$, N_2O_5, related trace gases, $PM_{2.5}$ and selected meteorological parameters for the study period. The data gaps were caused by technical problems, calibrations or maintenance~~s~~ of the instruments which usually took place in the afternoon of each day. Elevated $ClNO_2$ was measured in all of the 13 nights with full CIMS measurements which show typical night-time concentrations larger than 350 pptv. The highest $ClNO_2$ was observed on 20-21 June with maximum mixing ratio of 2070 pptv. There were several nights when $ClNO_2$ mixing ratios were less than 200 pptv (e.g. on 24-25, 28-29 June, and 8-9 July). The observed $ClNO_2$ levels at Wangdu are comparable with previous measurements made in both coastal (e.g. Osthoff et al., 2008; Riedel et al., 2012; Mielke et al., 2013) and inland sites (e.g. Thornton et al., 2010; Phillips et al., 2012; Riedel et al., 2013). As for N_2O_5, low concentrations (<200 pptv) were observed in every night, implying fast loss of N_2O_5, except in the night of 28-29 June when mixing ratio of up to 430 pptv were observed in the air masses with low humidity (RH = ~40%) and NO (<2 ppbv).

The observation of elevated $ClNO_2$ is in-line with the expectation of ubiquitous $ClNO_2$ precursors like NO_x, O_3 and aerosols in the NCP environment. As shown in Figure 2, afternoon mixing ratios of O_3 exceeded 90 ppbv on a majority of days, with a maximum value of 146 ppbv, indicative of intense photochemical reactions during the study period. NO_x mixing ratios were in the range of 10-80 ppbv, which reflects strong emissions of NO_x in the region. Similarly, aerosol loading was quite high, with $PM_{2.5}$ mass concentration larger than 60 µg m^{-3} on most of the days, with the highest value of 220 µg m^{-3}.

Figure 3 shows the 12-h backward particle dispersion trajectories with 08:00 local time (LT) as the starting time during 21 June – 9 July 2014. There were no significant changes in the origins of air masses for those trajectories arriving at 00:00 and 14:00 (Fig. ~~S3~~ S5 and ~~S4~~S6). The study period can be meteorologically separated into three parts. The first part, 21-23 June, indicates air masses from megacities of Beijing and Tianjin (passing over Baoding) in the northeast. The highest $ClNO_2$ level was observed in this period. The second part begins at 24 June and ends 7 July with large majority of air masses originating from the southern sector and passing over a portion of urban areas of Shijiazhuang. The $ClNO_2$ mixing ratios were in the range of tens of pptv to 1.2 ppbv. The final part is 8-9 July with air masses mostly from the less developed mountainous areas in the northwest sector, and the $ClNO_2$ concentrations were low. The entire field campaign was therefore dominated by air masses from southern regions, which is the typical summertime condition in the NCP.

3.2 Diurnal variations

Figure 4a illustrates the mean diurnal variation of $ClNO_2$ and relevant chemical data during the campaign. $ClNO_2$ exhibited a clear diurnal cycle with accumulation of $ClNO_2$ after sunset (~20:00) and reached a peak at ~08:00 in the morning. It then declined gradually to concentrations near the detection limit at noon. The average mixing ratios of $ClNO_2$ were up to 550 pptv. Its precursors, N_2O_5, only showed a small peak right after sunset with maximum average mixing ratio of 80 pptv, and remained at levels near the detection limit of the CIMS for the rest of the night. The NO_y, NO_x and S_a also showed a similar pattern as $ClNO_2$. They increased at sunset with average nighttime concentration of 29 ppbv, 21 ppbv and 1880 $\mu m^2\ cm^{-3}$, respectively, and were at lowest levels in mid-day. The average night-time NO_x to NO_y ratio was 0.72. Diurnal variation of O_3 was anti-correlated with that for NO_x, with the former concentration rapidly decreasing as night falls.

The highest mixing ratio of $ClNO_2$ was observed on 20-21 June in the outflow of Tianjin megacity (see Fig. 3). We termed it as the megacity case in the remaining of the paper. The $ClNO_2$ mixing ratios in the megacity case were in the range of 110 to 2070 pptv, while N_2O_5 peaked at 170 pptv (Figure 4b). NO_y, O_3 and S_a were generally at similar levels with the average condition, but the NO_x was less abundant at this night compared to the campaign average, with a mean value of 16 ppbv. Smaller NO_x/NO_y ratio of ~0.55 were found on this night, indicating more aged air masses being sampled.

3.3 Factors affecting $ClNO_2$ production

In this section, we examine the factors that may have caused the large difference of $ClNO_2$ levels in the megacity case and campaign average. Ambient $ClNO_2$ concentrations are affected by several factors including 1) production rate of NO_3 ($P(NO_3)$), 2) N_2O_5 reactivity (i.e. heterogeneous loss on aerosol surface, homogeneous reaction and dissociation to NO_3) and 3), production yield of $ClNO_2$ (ϕ). The calculated nighttime $P(NO_3)$ through R1, $P(NO_3) = k_{NO2+O3}[NO_2][O_3]$, do not show much difference, with 1.7 ± 0.6 ppbv h^{-1} in campaign average and 1.3 ± 0.5 ppbv h^{-1} in the megacity case. ~~Estimation of ϕ from the laboratory parameterization with measured aerosol chloride content (Roberts et al., 2009; Bertram and Thornton, 2009) give a comparable ϕ of ~0.7 in the two cases.~~

The N_2O_5 reactivity was assessed with inverse N_2O_5 steady state lifetime analysis by using Eq (1) and (2) below (e.g. Platt et al., 1984; Brown et al., 2003, 2006, 2009, 2016).

$$\tau(N_2O_5)^{-1} = \frac{P(NO_3)}{[N_2O_5]} = \frac{k(NO_3)}{K_{eq}[NO_2]} + k(N_2O_5)_{het} \quad \text{(Eq 1)}$$

~~$+ k_{Homo}$~~

$$k(NO_3) = k_{NO+NO3}[NO] + \sum_i k_i\,[VOC_i] \quad \text{(Eq 2)}$$

The steady state inverse lifetimes of N_2O_5, $\tau(N_2O_5)^{-1}$, is the sum of the N_2O_5 loss rate through NO_3 (i.e. $k(NO_3)/K_{eq}[NO_2]$), and N_2O_5 heterogeneous loss rate coefficient ($k(N_2O_5)_{het}$) ~~and gas phase reaction of N_2O_5 with water vapor (k_{Homo})~~ (see Eq 1). The total reactivity can be obtained by the ratio of $P(NO_3)$ to the observed N_2O_5 mixing ratios (Brown et al., 2009). K_{eq} is the temperature-dependent equilibrium coefficient in R5, and the $k(NO_3)$ is the loss rate coefficient of NO_3 with NO and VOCs (see Eq2). Thus $k(N_2O_5)_{het}$ can be obtained by subtracting $k(NO_3)/K_{eq}[NO_2]$ and k_{Homo} from the determined $\tau(N_2O_5)^{-1}$. We only conduct analysis for the period between ~20:30 (0.5 h after sunset) until ~23:30 when there were ~~was~~ no significant NO plumes (refer Figure 4), as interception of fresh emissions could lead to the failure of the N_2O_5 steady-state approximation in the air mass (e.g. Brown et al. 2003, 2011, 2016).

Figure 5a shows the averaged total N_2O_5 reactivity and fractions of N_2O_5 loss through NO_3~~,~~ ~~homogeneous~~ and heterogeneous loss of N_2O_5 for both campaign average and the megacity case. The determined $\tau(N_2O_5)^{-1}$ is 1.3 x 10^{-2} s^{-1} for campaign average and 5.8 x 10^{-3} s^{-1} for the megacity case, suggesting that the average total loss rate coefficient of N_2O_5 is twice of that of the megacity case. However, the N_2O_5 reactivity is mainly dominated by loss via NO_3 (89%) for the campaign average, which is in-line with its relatively higher VOCs and NO background (Fig. ~~S5~~S7). For the megacity case, although it has lower total N_2O_5 reactivity, the $k(N_2O_5)_{het}$ has about equal contribution with the loss via NO_3 and is about a factor of 2.4 faster than the campaign average. This gives a larger N_2O_5 uptake coefficient (γ) of 0.030 in the megacity case compared to 0.014 in the campaign average (which is estimated from equation 3, where c_{N2O5} is the mean molecular speed of N_2O_5).

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

~~The $ClNO_2$ production rate depends on the N_2O_5 heterogeneous loss rate coefficient, mixing ratios of N_2O_5 and ϕ, which~~ The $ClNO_2$ yield that best fits the observations can be estimated ~~predicted with equation (3) when the loss of $ClNO_2$ is negligible during the night-time~~ by dividing the $ClNO_2$ concentration over the integrated amount of N_2O_5 uptake loss, as shown in equation (4).

~~$\frac{d[ClNO_2]}{dt} = k(N_2O_5)_{het}[N_2O_5]\phi$~~

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

(Eq ~~3~~4)

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

The $ClNO_2$ production rate depends on the N_2O_5 heterogeneous loss rate coefficient, mixing ratios of N_2O_5 and ϕ, which can be predicted with equation (5) when the loss of $ClNO_2$ is negligible during the night-time.

$$\frac{d[ClNO_2]}{dt} = k(N_2O_5)_{het}[N_2O_5]\phi \qquad \text{(Eq 5)}$$

As illustrated in Figure 5b, the predicted $ClNO_2$ production rate is a factor of 4 larger than the campaign average. The larger $ClNO_2$ production rate can be justified by the twice higher $k(N_2O_5)_{het}\phi$ and more abundant N_2O_5 (c.a. 2 times larger) in the megacity case that was due to the less N_2O_5 loss through conversion to NO_3 (as shown above). This result is consistent with the observed fourfold higher $ClNO_2$ mixing ratios in the megacity case compared to the average condition (c.f. Fig. 4), demonstrating that the faster heterogeneous N_2O_5 loss and smaller loss via NO_3 in the megacity case were the major reasons contributing to the larger $ClNO_2$ concentrations.

3.4 Sustained $ClNO_2$ morning peaks

A distinct feature of the $ClNO_2$ is the elevated concentrations sustained after sunrise. Figure 6 depicts the expanded view of the morning $ClNO_2$ peaks together with related chemical characteristics in the campaign average and megacity case. $ClNO_2$ concentration continued to increase after sunrise (at ~04:40) and persisted for 4 hours from sunrise for almost every day. The average mixing ratio of the morning $ClNO_2$ peak was 550 pptv with the megacity case reaching ppbv level. These results are different from the typical diurnal patterns of $ClNO_2$ observed at other places, which usually show a decline of $ClNO_2$ levels at sun rises (e.g. Osthoff et al., 2008; Thornton et al., 2010; Mielke et al., 2013; Tham et al., 2014). As outlined in the introduction, morning ~~peak~~ peaks of $ClNO_2$ ~~was~~ were also observed in London (Bannan et al., 2015) and Texas (Faxon et al., 2015), but they were much smaller than the values at Wangdu.

3.4.1 Causes of $ClNO_2$ morning peaks

The $ClNO_2$ enhancement ($\Delta ClNO_2$) in the morning could be caused by in-situ $ClNO_2$ production and/or downward mixing of the $ClNO_2$ which has been produced in the residual layer (RL) over the night. We calculated the in-situ production of $ClNO_2$ (the area shaded in light grey in the Fig. 6) by using equation (~~4~~6), which is similar to equation (3), with additional consideration of $ClNO_2$ loss via photolysis. Since the $k(N_2O_5)_{het}$ and ϕ determined earlier (in section 3.3) are no longer applicable during the daytime, the N_2O_5 heterogeneous loss rate here was estimated from equation (~~5~~7), where γ is the N_2O_5 uptake coefficient and c_{N2O5} is the mean molecular speed of N_2O_5.

$$\frac{d[ClNO_2]}{dt} = k(N_2O_5)_{het}[N_2O_5]\phi - j_{ClNO2}[ClNO_2] \qquad \text{(Eq ~~4~~6)}$$

$$k(N_2O_5)_{het} = \frac{1}{4} c_{N2O5} S_a \gamma \qquad \text{(Eq ~~5~~7)}$$

We used a γ of 0.03 and unity ϕ of 1.0 in the calculations. These numbers are considered as upper end values based on previous field studies (Brown et al., 2006; Bertram et al., 2009; ~~Reidel~~Riedel et al., 2013). As shown in the lower panel of Figure 6, the calculated $\Delta ClNO_2$ with $\gamma\phi = 0.03$ cannot reproduce the observed increases in $ClNO_2$. Larger $\gamma\phi$ of 0.06 - 0.09 would be needed, but such large uptake coefficients and yields are not supported by the currently available data in the literature. Therefore, we think that in-situ $ClNO_2$ production is not the main reason for the $ClNO_2$ morning peak.

Meteorological and chemical data point to the entrainment of $ClNO_2$ rich air aloft after sun rise as the cause of the $ClNO_2$ morning peaks. Figure 7 shows the fractions of air arriving at the measurements site from various altitudes at different time of day based on the simulations of WRF-HYSPLIT. Vertical mixing was limited prior to sunrise (~04:00) as most of the air masses were confined to ground level (< 200 m above ground level, a.g.l.). Shortly after sunrise (~05:00), contributions of air masses from the higher levels began to increase after the break-up of nocturnal boundary layer (NBL). As time advanced, larger fraction of higher-level air masses impacted the surface site. Chemical data is consistent with the meteorological analysis. As shown in Figure 6, the SO_2/NO_y ratios in both cases increased up to 0.6-0.8 after sunrise, indicative of the impact of plumes from coal-fired facilities like power plants. The power-plant plumes from elevated stacks typically reside above the nocturnal boundary layer (NBL) due to poor mixing at night. Coal-fired power plants emit large amount of NO_x and Cl^- containing aerosols, in addition to SO_2 (McCulloch et al., 1999; Zhao et al., 2008). Together with high O_3 produced in the preceding daytime and aerosol loadings, significant production of $ClNO_2$ above the NBL are expected and indeed have been observed in previous field studies (Wagner et al., 2012; Young et al., 2012; Riedel et al., 2013). In the present study, the $ClNO_2$ precursors like Cl^- aerosol and $P(NO_3)$ and a co-product of chlorine activation, nitrate (NO_3^-) aerosol also showed significant enhancement in the early morning hours (see Fig. 6).

3.4.2 Estimation of $ClNO_2$ concentrations in the residual layer

We estimate the amount of the $ClNO_2$ that would exist in the residual layer to maintain the observed $ClNO_2$ at ground level. Here we use a simplified one dimensional (1-D) model to illustrate the mixing process. This model contains two layers of air before sunrise; NBL and RL, with $ClNO_2$ concentrations of C_n and C_r, respectively (see Fig. ~~S6~~S8). We assume no mixing of air masses (and $ClNO_2$) between the two layers. After sunrise, the two layers are efficiently mixed, yielding a constant concentration of $ClNO_2$ (C_p). The heights of the daytime planetary boundary layer (PBL) and NBL were calculated by the WRF model, which has been previously demonstrated to be capable of reproducing the PBL heights with a bias of about -13% (Hu et al., 2010). The difference in the heights of PBL and NBL is the depth of the RL. C_n and C_p are the observed mixing ratios before (at 05:00) and after (at 08:00) sunrise, respectively. The concentration in RL layer before sunrise can be estimated by the mass balance approach taking consideration of loss of $ClNO_2$ from photolysis between 05:00 and 08:00 (Eq (~~6~~8)).

$$C_p \times H_p = (C_n \exp^{(-j_{ClNO2}t)} \times H_n) + (C_r \exp^{(-j_{ClNO2}t)} \times H_r)$$

(Eq ~~6~~8)

Where j_{ClNO2} is photolysis rate of $ClNO_2$ and t is time. The estimated $ClNO_2$ concentration in the RL may subject to underestimation due to the omission of the upward diffusion of $ClNO_2$ in the RL to the free troposphere.

For the campaign average, WRF calculated boundary layer height is 30 m and 325 m (a.g.l.) at 5:00 and 8:00, respectively (refer to Fig. ~~S7~~S9). This gives a mixing ratio of $ClNO_2$ in the RL of 1.7 ppbv. For the megacity case with boundary layer height of 72 m at 05:00 and 610 m at 08:00, the $ClNO_2$ in the RL by sunrise would be 4.0 ppbv. The uncertainties of the simulated boundary layer heights may affect the calculated $ClNO_2$ concentration. Recalculation of the $ClNO_2$ concentration by increasing the simulated nocturnal boundary layer height (05:00) by a factor of 2 while remaining the same boundary layer height at 08:00 shows a difference in calculated $ClNO_2$ of less than 10%. These estimated $ClNO_2$ concentrations~~values~~ are within the range of aircraft and tower measurements in RL in the US (Wagner et al., 2012; Young et al., 2012; Riedel et al., 2013) and are comparable to the highest $ClNO_2$ observed at a mountain site in southern China (Wang et al., 2016). ~~This~~ These results suggest that elevated $ClNO_2$ may be frequently ~~always~~ present in the residual layer of this region.

3.5 Sources of chloride aerosols

The elevated $ClNO_2$ at Wangdu site requires sufficient amount of chloride aerosols to support its production. ~~Abundance~~ Abundant ~~of~~ fine Cl^- aerosols ~~were~~ was frequently observed during night hours (20:00-09:30) with a mean concentration of 1.6 μg m^{-3} and maximum of 6.8 μg m^{-3} (Fig. 8). The presence of gas-phase HCl during the night (mean = 0.78 ppbv) also can continuously replenish the Cl^- aerosol. The Cl^- concentrations in our study are comparable to those previously observed in the NCP (Sun et al., 2006; Huang et al., 2014; Sun et al., 2015). As can be seen in Figure 3, back-trajectories at Wangdu indicated the air was mainly of continental origins with limited direct influences from the oceans. Chemical data also provide evidence for non-oceanic Cl^- sources. The Cl^- aerosol showed good correlation (r >0.75) with SO_2 in 11 out of 16 nights, including 4 nights with concurrent good correlation (r >0.75) with a biomass burning tracer of acetonitrile (CH_3CN) (see Table 2). These results suggest that coal-fired power plants are a dominant source of chloride in the region with additional contributions from biomass burning. Significant chlorine content (260 mg kg^{-1}) has been found in the coal used in China (Zhang et al., 2012). Under high temperature and oxygen free conditions, combustion of coal can release up to 97% of the chlorine in the coal in the form of HCl gas (Gibb, 1983) which can then be transformed into aerosol phase (Cl^-) through neutralization reactions in the ambient air. The contribution of biomass burning at Wangdu can also be seen in the active fires data on the nights with good correlation between Cl^- aerosol and CH_3CN. Figure 9 shows an example of burning activities mostly in south of Wangdu on 28-29 June. Li et al. (2007) measured composition of smoke from burning of wheat straw and maize stover harvested in NCP and found 13.8% and 23.0% of Cl^- in the $PM_{2.5}$ mass loading, respectively. Recent field measurement of biomass burning plumes during the harvesting period in China also indicated a drastic increase in the Cl^- concentration (>20 μg m^{-3}) (J. F. Li et al., 2014).

3.6 The impact of $ClNO_2$ on primary radical and ozone production

This section examines the contributions of $ClNO_2$ to the primary RO_x ($OH+HO_2+RO_2$) radical and in-situ ozone production at Wangdu using the observation-constrained box model described in Section 2.5. The analysis focuses on campaign average condition and the megacity case. The mean concentrations of trace gases and other parameters that serve as inputs are shown in Table S2.

Figure 10a illustrates the Cl production rate derived from the photolysis of $ClNO_2$ and without $ClNO_2$ (only from photolysis of Cl_2 and HCl+OH). It shows that photolysis of $ClNO_2$ was the predominant source of Cl in Wangdu compared to the reaction of HCl and OH and photolysis of Cl_2. The production of Cl was efficient in the morning (from sunrise to ~11:00) and reached maximum at ~08:00 corresponding to the peak concentration of $ClNO_2$. The Cl production rate was up to 0.24 ppbv h^{-1} for average condition, and up to 1.12 ppbv h^{-1} for the megacity case. Figure 10b depicts the primary daytime RO_x production ($P(RO_x)$) from sources including photolysis of $ClNO_2$, OVOCs (excluded HCHO), HCHO, HONO and O_3 (O^1D+H_2O), O_3+VOCs, and NO_3 oxidation~~s~~. Similar to ~~other~~ previous studies, the primary daytime $P(RO_x)$ is dominated by sources from photolysis of HCHO, OVOCs and HONO (Kanaya et al., 2009; Liu et al., 2012; Lu et al., 2013). The photolysis of $ClNO_2$ is particularly important during the morning hours. During 08:00 - 08:30, photolysis of $ClNO_2$ contributed to 10% of the $P(RO_x)$ on average condition and with a much larger contribution of 30% in the megacity case. These results highlight the importance of $ClNO_2$ as a significant source of RO_x radicals in this region. Reader is referred to Z. Tan et al., (2016, submitted to this issue of Atmospheric Chemistry and Physics) for more extensive analysis on the RO_x chemistry at Wangdu.

The effect of $ClNO_2$ photolysis on in-situ ozone production is also relevant. Figure 11 shows the net ozone production rates ($P(O_3)$) during daytime (from 05:00 to 18:00) and the difference ~~of~~ in integrated total ozone production simulated with $ClNO_2$ and without $ClNO_2$ input. The O_3 production rates were enhanced throughout the day due to the $ClNO_2$ effect, especially during the morning hours. The increase ~~of~~ in net $P(O_3)$ for campaign average reached 0.9 ppbv h^{-1} or 17% during the morning. For the megacity outflow, much higher increases in $P(O_3)$ can be seen in the entire morning, with a maximum of 3.3 ppbv h^{-1} (or 76% increase) at ~08:00. Integrating over the entire daytime period, the increase ~~of~~ in total ozone production was 4.3 ppbv (3%) and 11 ppbv (13%) for average condition and the megacity case, respectively. Although not directly comparable, these values are generally within the range of net ozone production increase caused by $ClNO_2$ in previous studies in Houston (Osthoff et al., 2008), Los Angeles (Riedel et al., 2014), and southern China (Xue et al., 2015; Wang et al., 2016).

We notice a large difference in the impact of $ClNO_2$ on ozone production between campaign average and the megacity case. This can be explained by their different $ClNO_2$ and VOCs characteristics. First, for campaign average, the $ClNO_2$ mixing ratio was much lower than that of the megacity case (see section 3.3). The smaller $ClNO_2$ concentrations, in turn, would produce less chlorine radical in the daytime, reducing the production of RO_x which ultimately decreases the O_3 production. A simulation test by only reducing the $ClNO_2$ mixing ratios in the megacity case by a factor of 2.8 (that is, to the same levels of campaign average) showed a sharp drop in the increase of the ozone production from 13% to 6% (Fig. ~~S8a~~S10a), confirming the importance of $ClNO_2$ mixing ratios in driving the ozone enhancement. Second, the higher OVOC to NMHC fraction in campaign average (see Fig. ~~S9~~ S11 for the VOCs mix) provided a larger pool of RO_x, and the radical propagation would amplify the OH through efficient radical recycling (Liu et al., 2012), dampening the effect of chlorine radical. Another test by only increasing the $ClNO_2$ mixing ratios in campaign average condition to the same value of the megacity case indicated a relatively smaller increase ~~of~~ in the ozone production (9%) (see Fig. ~~S8b~~S10b) compared to the increased percentage of O_3 production in the megacity case (13%).

The much higher OVOCs mixing ratios to NMHCs in campaign average are likely influenced by the biomass burning activities which are more intense in the regions south of Wangdu (refer to Fig. S1) and the biomass burning-influenced plumes can be transported to Wangdu by prevailing southerly winds as shown by the trajectories (Fig. 3). During our field measurement, we indeed observed significant increase (up to 170 ppbv) of OVOCs in a fresh biomass burning plume ~~on~~ at the midnight of 15 June 2014 (Fig. ~~S10~~S12). High content of OVOCs from biomass burning has been previously reported at a mountain–site of the NCP (Inomata et al., 2010). Significant emissions of OVOCs from the burning of Chinese crop residues were also reported in a recent laboratory study (Inomata et al., 2015).

We hence conclude that higher concentrations of $ClNO_2$ and lesser abundant of VOCs (i.e. smaller OVOC to NMHC fraction) in the megacity case resulted in a relatively higher impact of Cl chemistry on the ozone formation. Although we only measured very high $ClNO_2$ concentration in one event of megacity outflow, similar cases occurred in the beginning of the study period during which NO_x, NO_y, S_a and VOCs data were available (but not $ClNO_2$). An examination of the VOCs mix and other chemical compounds confirmed the less abundance of OVOCs but has similar chemical characteristics in these cases (see Fig. S11 for an example of chemical characteristics on 23 and 27 June 2014). Previous studies have shown less abundance of OVOCs relative to NMHCs in and downwind of urban Beijing (Liu et al., 2009; Xu et al., 2011). Thus, we suggest that the effect of $ClNO_2$ on ozone enhancement may be more important in air masses dominated by urban/power plants emissions than those by biomass burning.

4. Summary and conclusions

This first $ClNO_2$ measurement in northern China unambiguously documented the presence of elevated $ClNO_2$ in this highly polluted region. Highest $ClNO_2$ mixing ratio (2070 pptv, 1 min average) was observed in an urban outflow plume on 20-21 June 2014. The air mass was characterized by faster (by a factor of 2.4) N_2O_5 heterogeneous loss as well as larger $ClNO_2$ production rate (by a factor of 4) compared to campaign average condition. The peak concentrations of $ClNO_2$ often occurred

4 hours after sun rise. Downward mixing of $ClNO_2$ rich air in the residual layer is believed to be the cause of these morning peaks, and the mixing ratios of $ClNO_2$ in ~~RL~~ residual layer are estimated in the range of 1.7-4.0 ppbv. These values are supported by our mountain-top measurement of $ClNO_2$ in Hong Kong with mixing ratio of up to 4.7 ppbv in well processed urban/industrial plumes (Wang et al., 2016). The Wangdu result implies strong productions of $ClNO_2$ in the residual layers over the polluted regions of northern China. We also ~~present~~ observed evidence for existence of fine aerosol chloride from non-oceanic sources like coal-fired power plants and burning of crop residues, suggesting the widespread effects of $ClNO_2$ on the oxidative capacity and production of secondary pollutants in this region. Our model calculations suggest a larger impact of $ClNO_2$ on primary radical productions and ozone enhancement in urban/power plant emission dominated air masses compared to biomass burning due to higher levels of VOCs (also larger OVOC to NMHC ratios) and relatively lower $ClNO_2$ in the latter case ~~reducing the effect of $ClNO_2$~~. More studies in non-biomass burning seasons and in areas adjacent to megacities/power plants are needed to examine the production of $ClNO_2$ and its effect on ~~the~~ regional photochemistry. Vertical profile measurements of $ClNO_2$ and related species would ~~also~~ be highly desirable.

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Table 1. Measurement method for trace gases and aerosols.

Species	Measurement Techniques	Detection Limits	Uncertainty	Time resolution
$ClNO_2$, N_2O_5	CIMS	6-7 pptv	25%	1 min
O_3	UV photometry	0.5 ppbv	5%	1 min
NO	Chemiluminescence	0.06 ppbv	20%	3 min
NO_2	Photolytical converter & Chemiluminescence	0.3 ppbv	20%	1 min
NO_y	MoO catalytic converter & Chemiluminescence	<0.1ppbv	5%	1 min
CH_4	CRDs	0.1 ppmv	<5%	1 min
SO_2	Pulsed-UV fluorescence	0.1 ppbv	5%	1 min

CO	IR photometry	4 ppbv	5%	1 min
HONO	LOPAP	7 pptv	20%	0.5 min
HCl	GAC-IC	59 pptv	10%	30 min
NMHCs	GC-FID/MS	20 - 300 pptv	15-20%	60 min
OVOCs	PTR-MS	10 - 50 pptv	15%	5 min
Formaldehyde	Hantzsch (wet chemical fluorimetric)	25 pptv	5%	1 min
$PM_{2.5}$	TEOM	2 $\mu g/m^3$	10%	1 min
Aerosol ionic compositions	GAC-IC	0.01-0.16 $\mu g/m^3$	10%	30 min

~~Species~~	~~Measurement Techniques~~	~~Detection Limits~~	~~Time resolution~~
~~$ClNO_2$, N_2O_5~~	~~CIMS~~	~~6-7 pptv~~	~~1 min~~
~~O_3~~	~~UV photometry~~	~~0.5 ppbv~~	~~1 min~~
~~NO~~	~~Chemiluminescence~~	~~0.06 ppbv~~	~~3 min~~
~~NO_2~~	~~Photolytical converter & Chemiluminescence~~	~~0.3 ppbv~~	~~1 min~~
~~NO_y~~	~~MoO catalytic converter & Chemiluminescence~~	~~<0.1ppbv~~	~~1 min~~
~~CH_4~~	~~CRDs~~	~~0.1 ppmv~~	~~1 min~~
~~SO_2~~	~~Pulsed-UV fluorescence~~	~~0.1 ppbv~~	~~1 min~~
~~CO~~	~~IR photometry~~	~~4 ppbv~~	~~1 min~~
~~HONO~~	~~LOPAP~~	~~7 pptv~~	~~0.5 min~~
~~HCl~~	~~GAC-IC~~	~~59 pptv~~	~~30 min~~
~~NMHCs~~	~~GC-FID/MS~~	~~20 – 300 pptv~~	~~60 min~~
~~OVOCs~~	~~PTR-MS~~	~~10 - 50 pptv~~	~~5 min~~
~~Formaldehyde~~	~~Hantzsch (wet chemical fluorimetric)~~	~~25 pptv~~	~~1 min~~
~~$PM_{2.5}$~~	~~TEOM~~	~~2 $\mu g/m^3$~~	~~1 min~~

~~Aerosol ionic compositions~~	~~GAC-IC~~	~~0.01-0.16 µg/m^3~~	~~30 min~~

Table 2. Correlations of chloride with power plant and biomass burning indicators (from 20:00-09:30 LT).

Duration (20:00-09:30)	$[Cl^-]$	Power plant indicator (SO_2)			Biomass burning indicator (CH_3CN)		
	Mean (µg m^{-3})	Mean (ppbv)	Slope	Correlation (*r*)	Mean (ppbv)	Slope	Correlation (*r*)
20-21 June	1.450	5.74	0.092	0.858	0.35	2.20	0.330
21-22 June	2.792	3.87	0.267	0.963	*n/a*	*n/a*	*n/a*
23-24 June	1.729	5.65	0.234	0.946	0.43	0.10	0.003
24-25 June	0.760	4.88	0.235	0.852	0.39	36.96	0.547
25-26 June	1.988	2.79	0.281	0.833	0.56	11.27	0.893
27-28 June	0.335	6.67	0.008	0.213	0.39	-1.33	0.577
28-29 June	0.915	7.44	0.083	0.831	0.55	2.77	0.830
29-30 June	1.429	22.67	0.048	0.719	0.48	4.96	0.442
30 June – 1 July	1.283	10.43	0.094	0.781	0.45	6.01	0.268

01-02 July	0.762	2.53	0.089	0.630	0.32	4.76	0.448
02-03 July	2.187	3.84	0.195	0.762	0.43	10.68	0.548
03-04 July	2.636	3.69	0.314	0.613	0.39	12.76	0.566
04-05 July	2.158	2.55	0.365	0.922	0.35	30.09	0.924
05-06 July	2.857	7.29	0.112	0.776	0.44	12.86	0.763
06-07 July	1.720	6.04	0.113	0.853	0.46	9.84	0.502
07-08 July	1.939	8.70	0.084	0.607	0.49	2.14	0.157

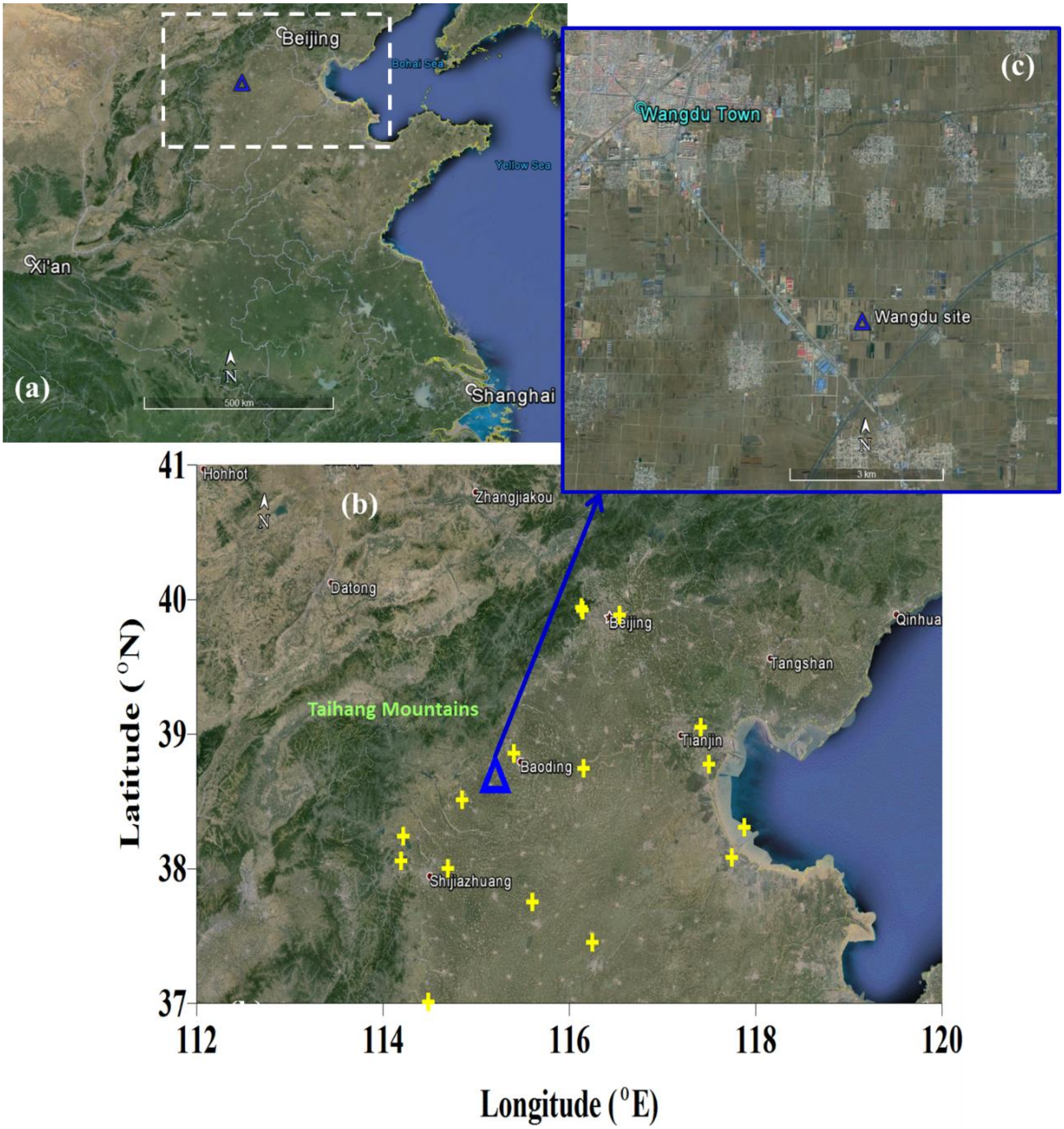
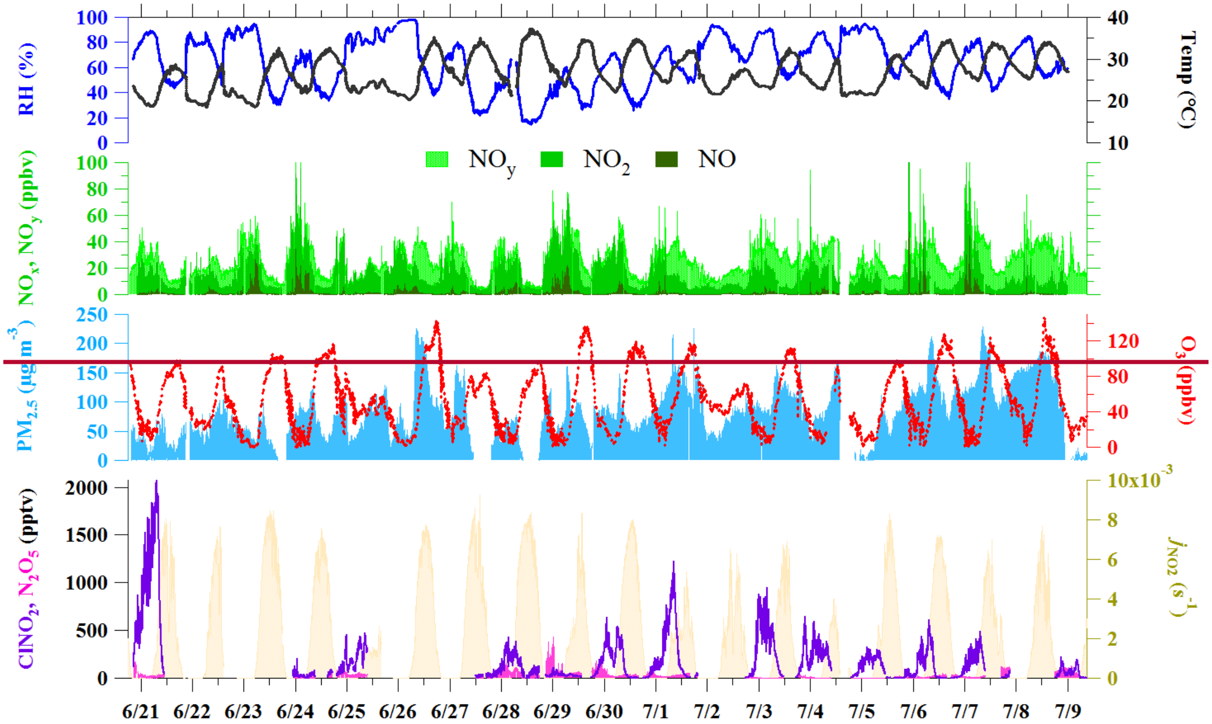


Figure 1. Google map showing a) the location of northern China (white dash-box) and Wangdu site (blue triangle), b) an expanded view of northern China plain with the topography, major cities and the locations of major coal-fired power plants (yellow cross) in the region, c) nearby environment of Wangdu site.


RH (%)
Temp (°C)
100
80
60
40
20
0
40
30
20
10
NOy
NO2
NO
NOx, NOy (ppbv)
PM2.5 (μg m-3)
250
200
150
100
50
O3 (ppbv)
120
80
40
ClNO2, N2O5 (pptv)
2000
1500
1000
500
jNO2 (s-1)
10x10-3
8
6
4
2
6/21
6/22
6/23
6/24
6/25
6/26
6/27
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7/6
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7/8
7/9

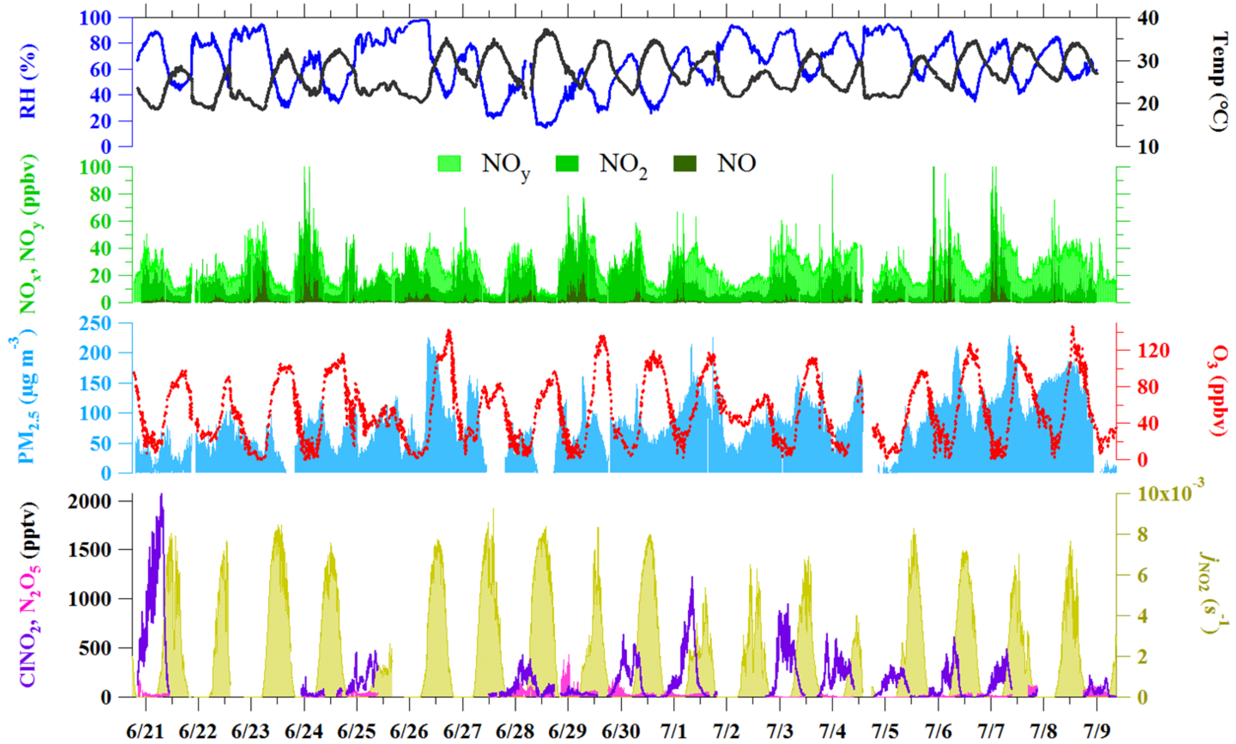

RH (%)
Temp (°C)
100
80
60
40
20
0
40
30
20
10
NOy
NO2
NO
NOx, NOy (ppbv)
PM2.5 (μg m-3)
250
200
150
100
50
O3 (ppbv)
120
80
40
ClNO2, N2O5 (pptv)
2000
1500
1000
500
jNO2 (s-1)
10x10-3
8
6
4
2
6/21
6/22
6/23
6/24
6/25
6/26
6/27
6/28
6/29
6/30
7/1
7/2
7/3
7/4
7/5
7/6
7/7
7/8
7/9

Figure 2. Time series of $ClNO_2$, N_2O_5 together with related species and meteorological data. Data are at 1-minute time resolution, except for NO_x data which are 5-minute averages.

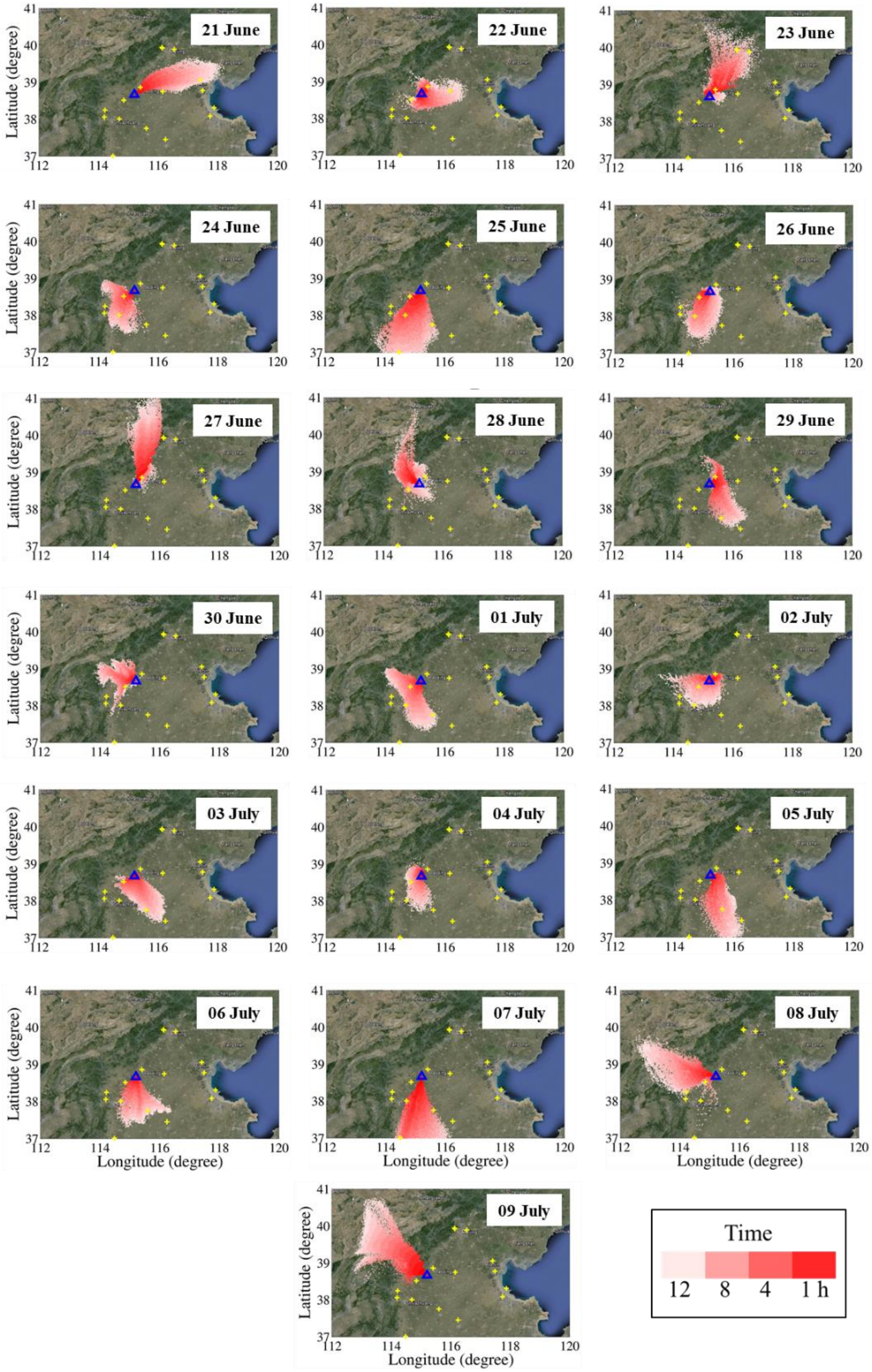


Figure 3. 12-hour history of air masses arriving at the measurement site at 08:00. Yellow cross represents major coal-fired power plants in the region.

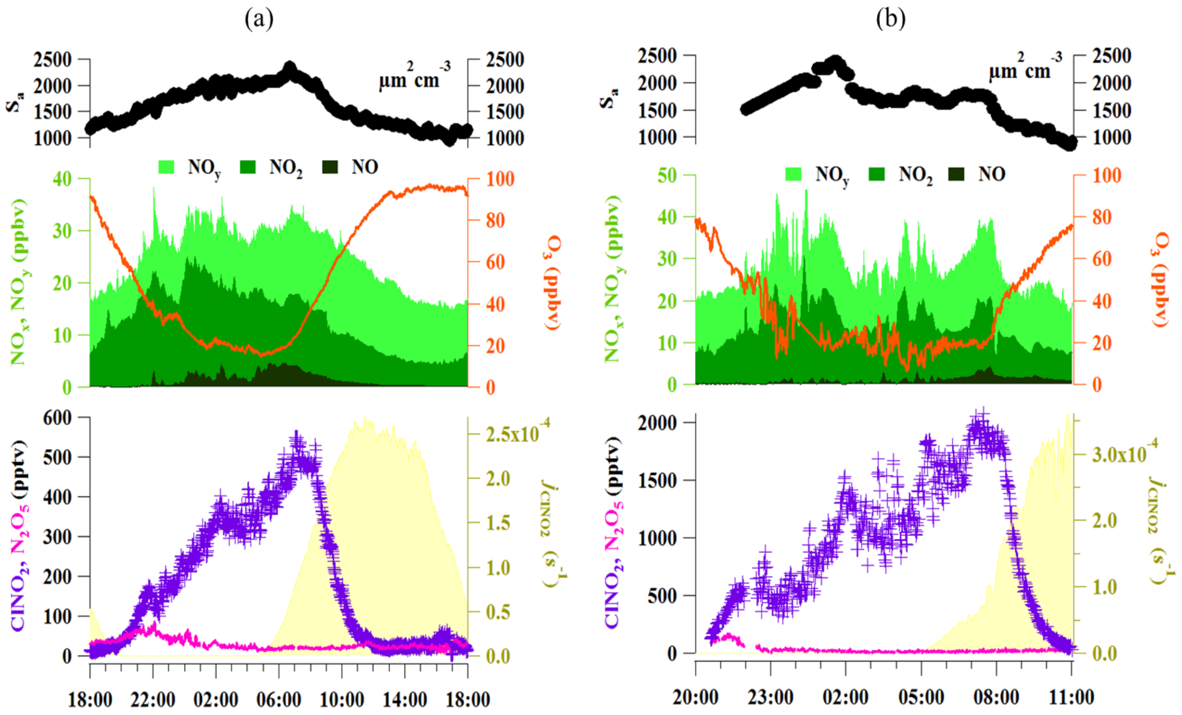
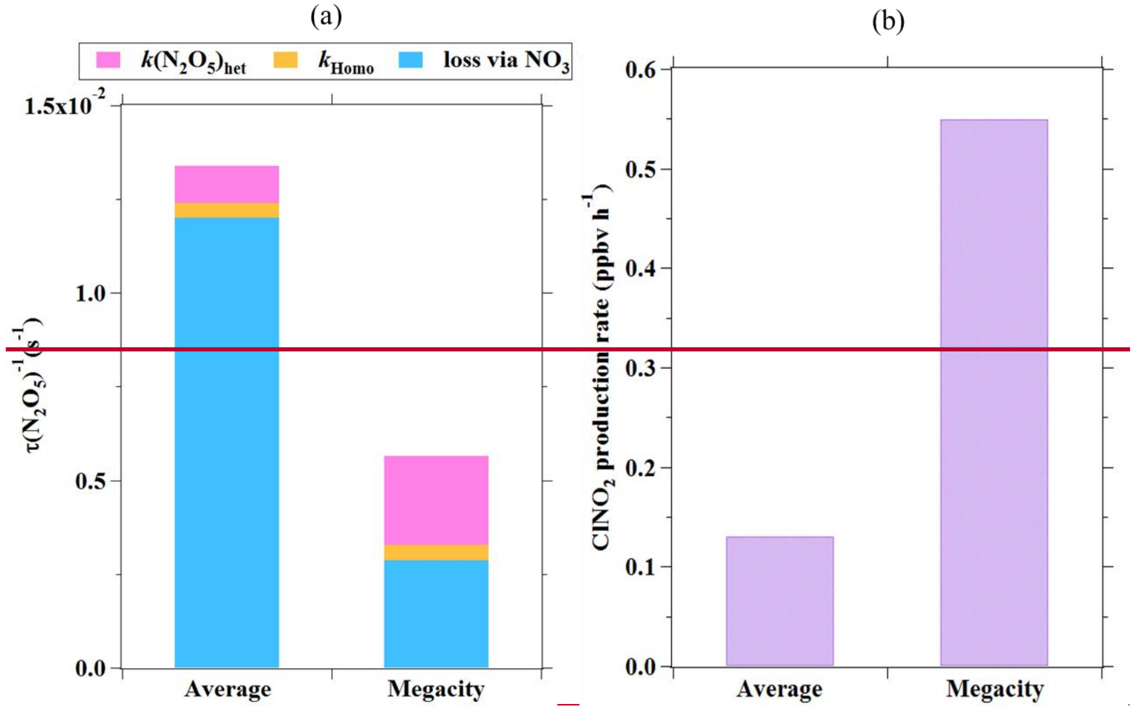


Figure 4. Diurnal variations of $ClNO_2$, N_2O_5, NO_x, NO_y, O_3 and particle surface area for a) campaign average (from 20 June to 9 July 2014 when $ClNO_2$ data is available) and b) the highest $ClNO_2$ case on 20-21 June 2014 (the megacity case).


(a)
(b)
$k(N_2O_5)_{het}$
k_{Homo}
loss via NO_3
$1.5x10^{-2}$
1.0
0.5
0.0
$\tau(N_2O_5)^{-1}$ (s^{-1})
Average
Megacity
0.6
0.5
0.4
0.3
0.2
0.1
0.0
$ClNO_2$ production rate (ppbv h^{-1})
Average
Megacity

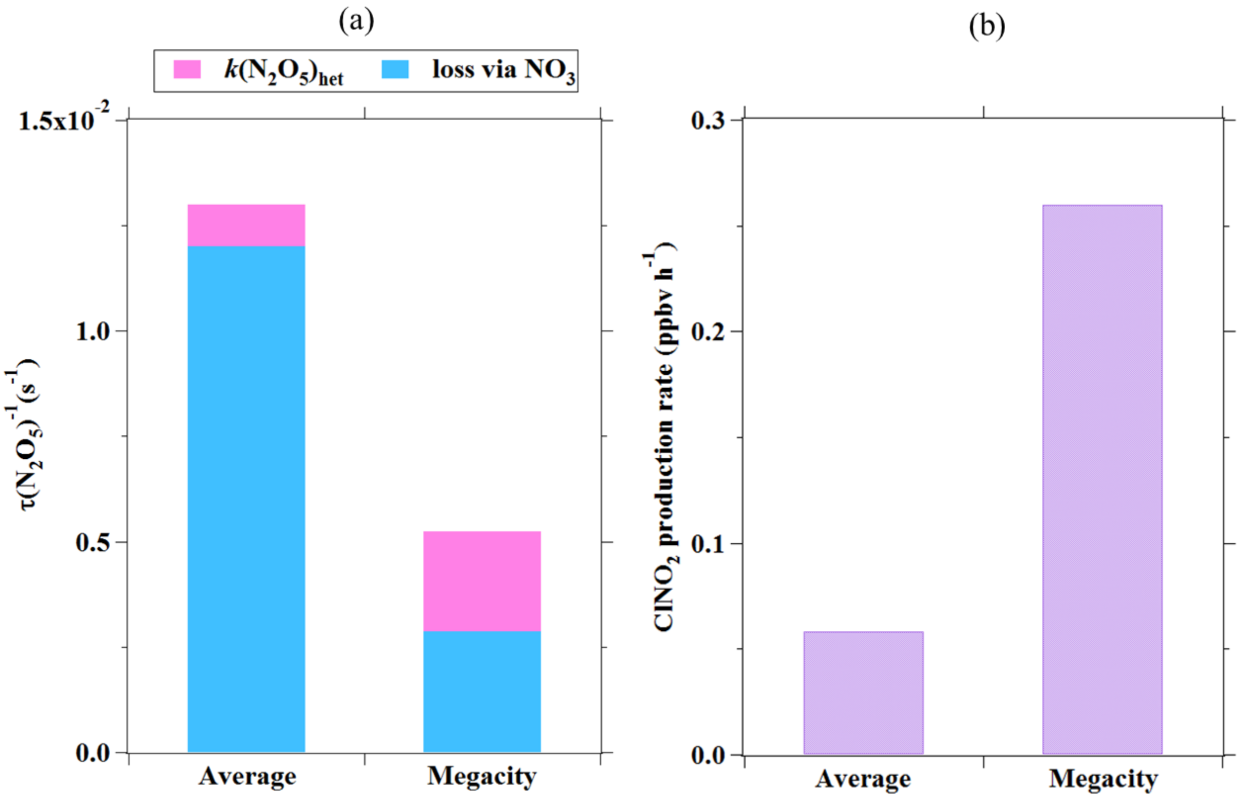


Figure 5. a)
Fractions of N_2O_5 loss rate coefficient through NO_3, homogenous and heterogeneous reaction of N_2O_5 for campaign average and the megacity case; b) the calculated $ClNO_2$ production rate for campaign average and the megacity case. 5 ~~The fractions of N_2O_5 loss rate coefficient through NO_3, homogenous and heterogeneous reaction of N_2O_5 for campaign average and the megacity case; b) the predicted $ClNO_2$ production rate in the megacity case shows to be fourfold larger than campaign average.~~

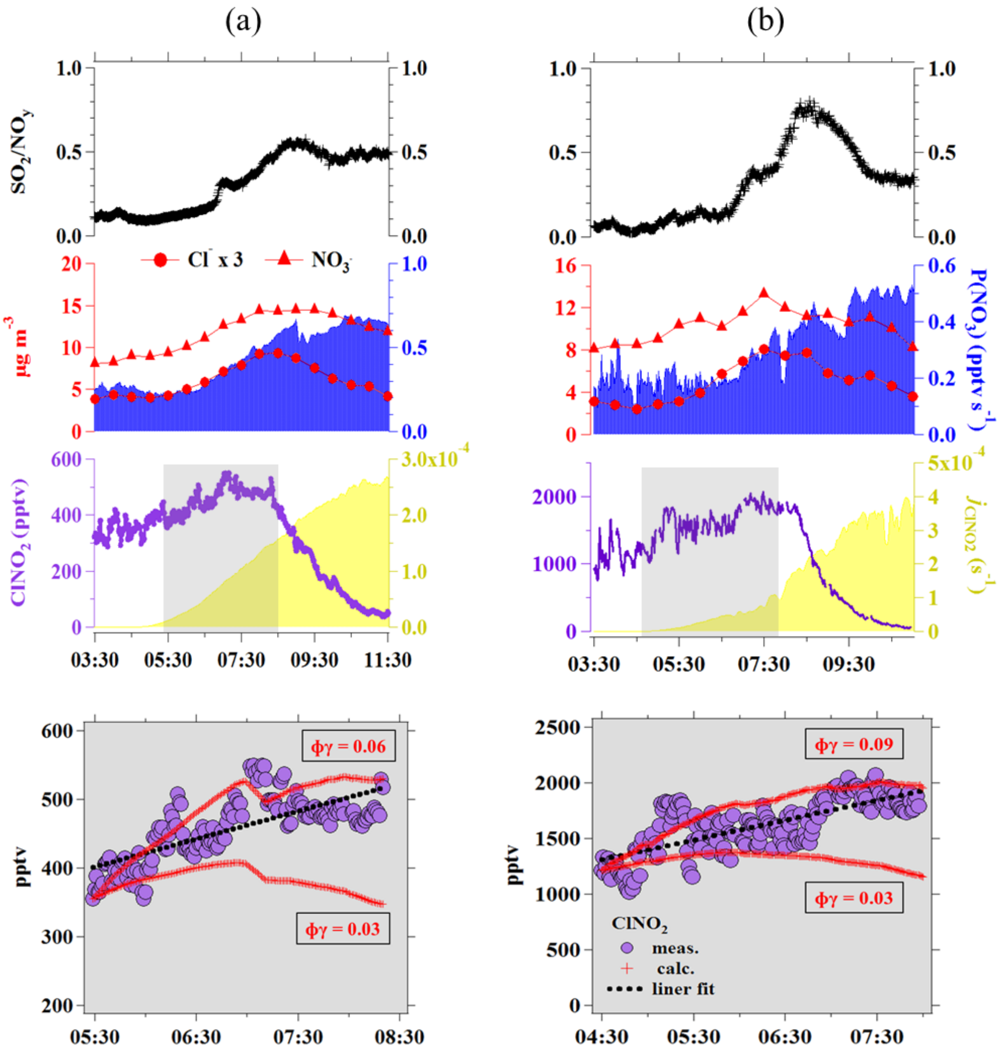


Figure 6. Expanded view of the sustained morning $ClNO_2$ peaks for a) campaign average and b) the megacity case. The upper panel shows some relevant chemical information including SO_2/NO_y, Cl^-, NO_3^-, and $P(NO_3)$. The increase of $ClNO_2$ in the shaded area (light grey) are compared to the calculated in-situ production of $ClNO_2$ (lower panel).

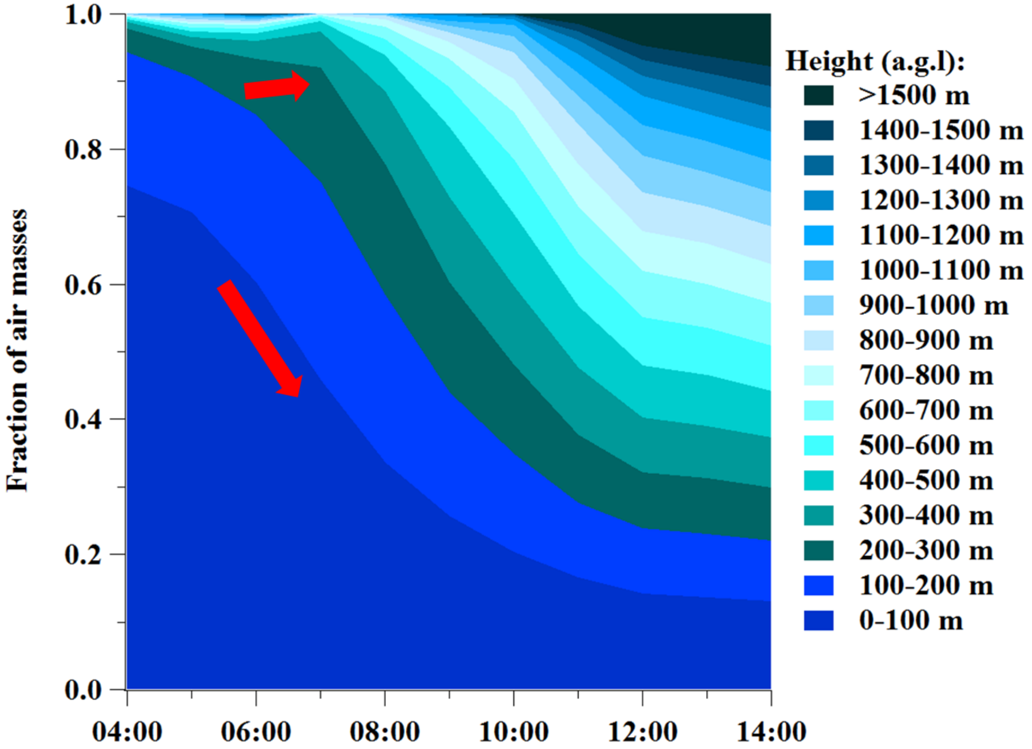


Figure 7. Fractions of air masses arriving at the measurement site at different time of the day (average condition). It is noted that these fractions were derived from the 1 h backward-in-time HYSPLIT simulation results. Red arrows show the decreased contribution of lower layer (<200m) and increased contribution from upper layer (>200m) air masses shortly after sunrise.

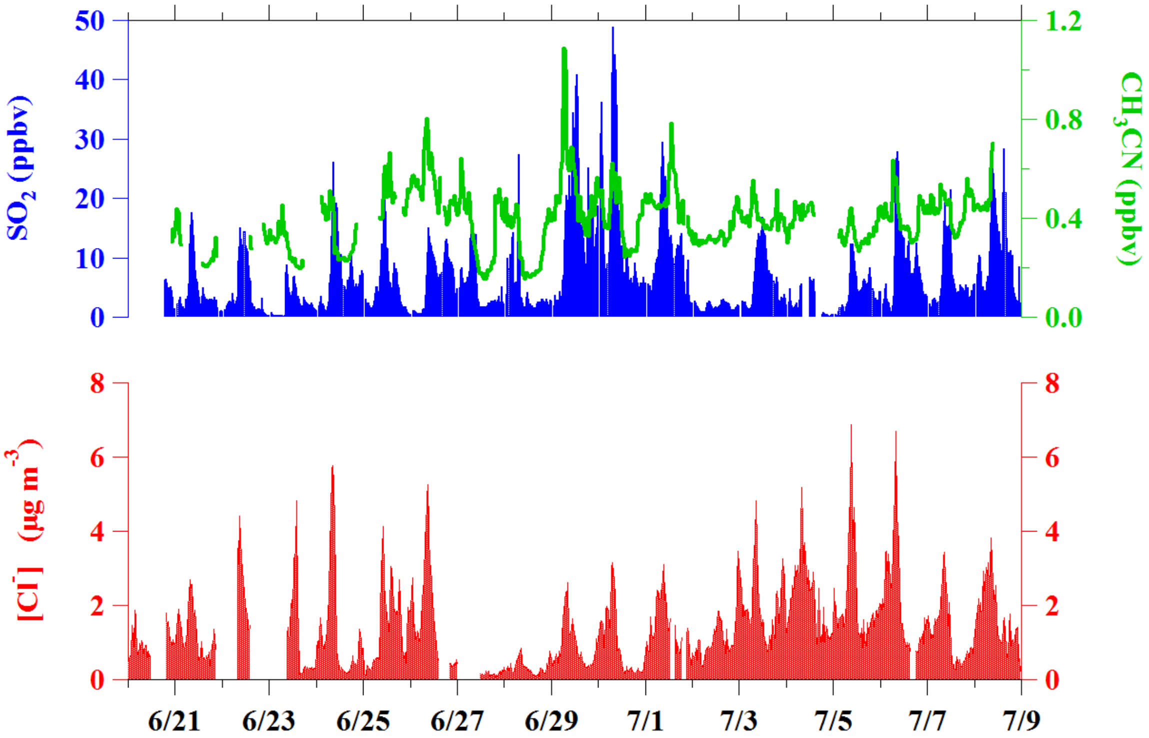


Figure 8. Time series of Cl$^-$ aerosol, SO$_2$ (a coal-fired power plant indicator) and CH$_3$CN (a biomass burning indicator) from 20 June to 9 July 2014.

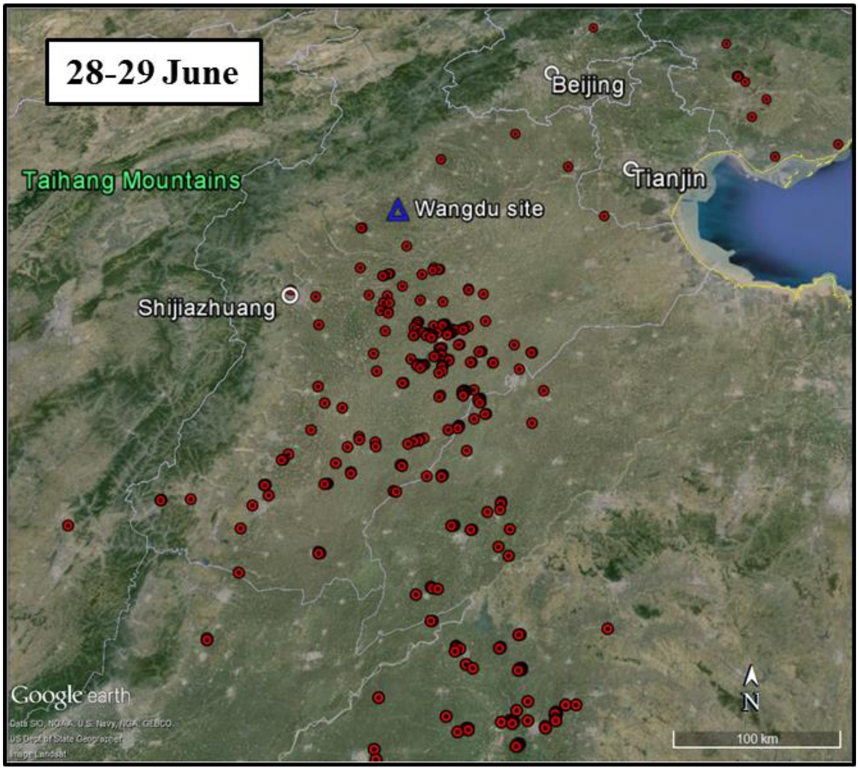


Figure 9. Biomass burning activities from the active fire hotspots data (red dots) on 28-29 June 2014 (Data available at https://earthdata.nasa.gov/firms).

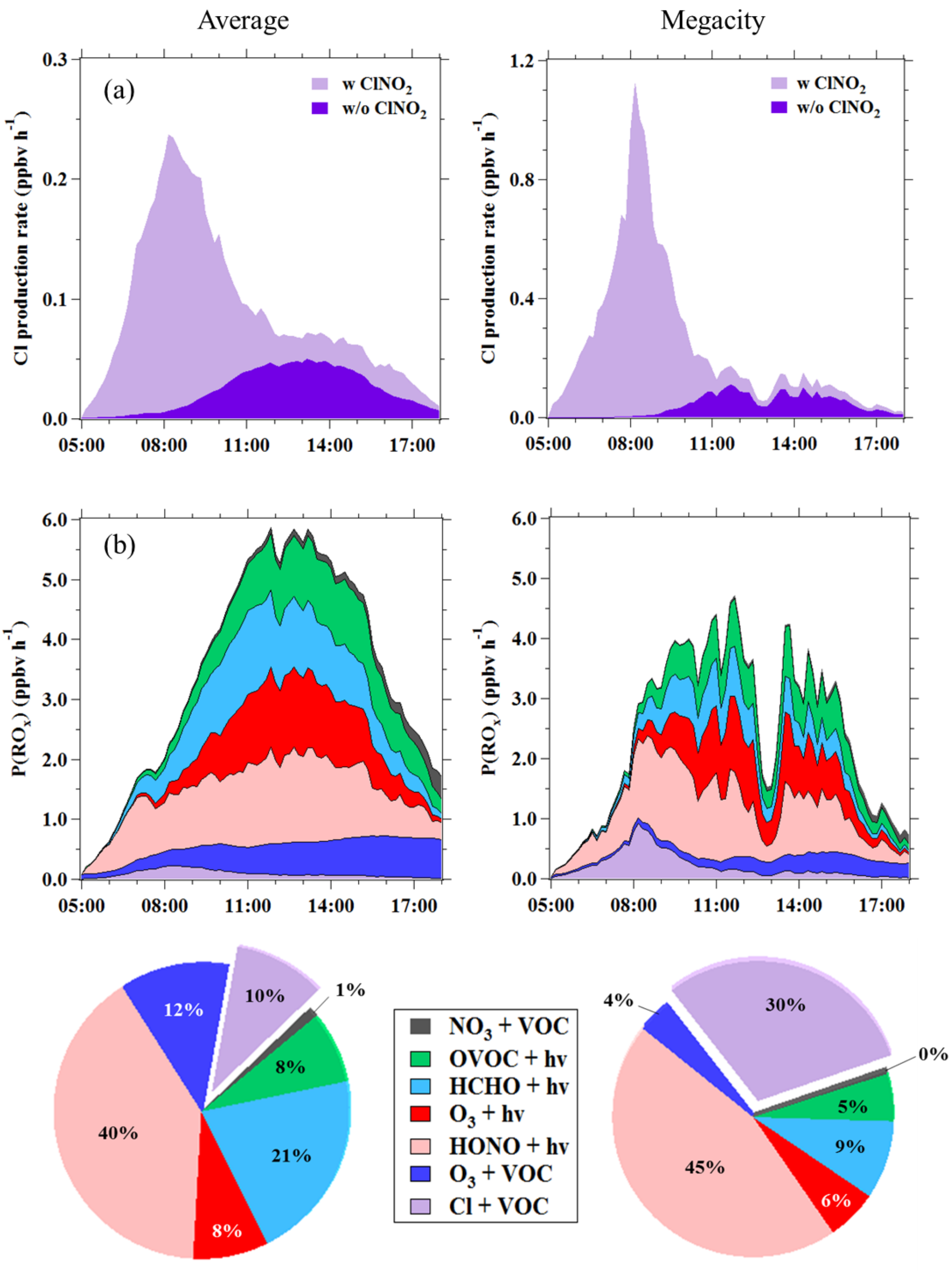


Figure 10. a) Cl production rates with ClNO$_2$ and without ClNO$_2$ input; b) primary RO$_x$ radical production rates from different sources at Wangdu in the daytime. Pie charts represent the contributions of ClNO$_2$ to the primary RO$_x$ radical production in the morning time (average value for 08:00-08:30).

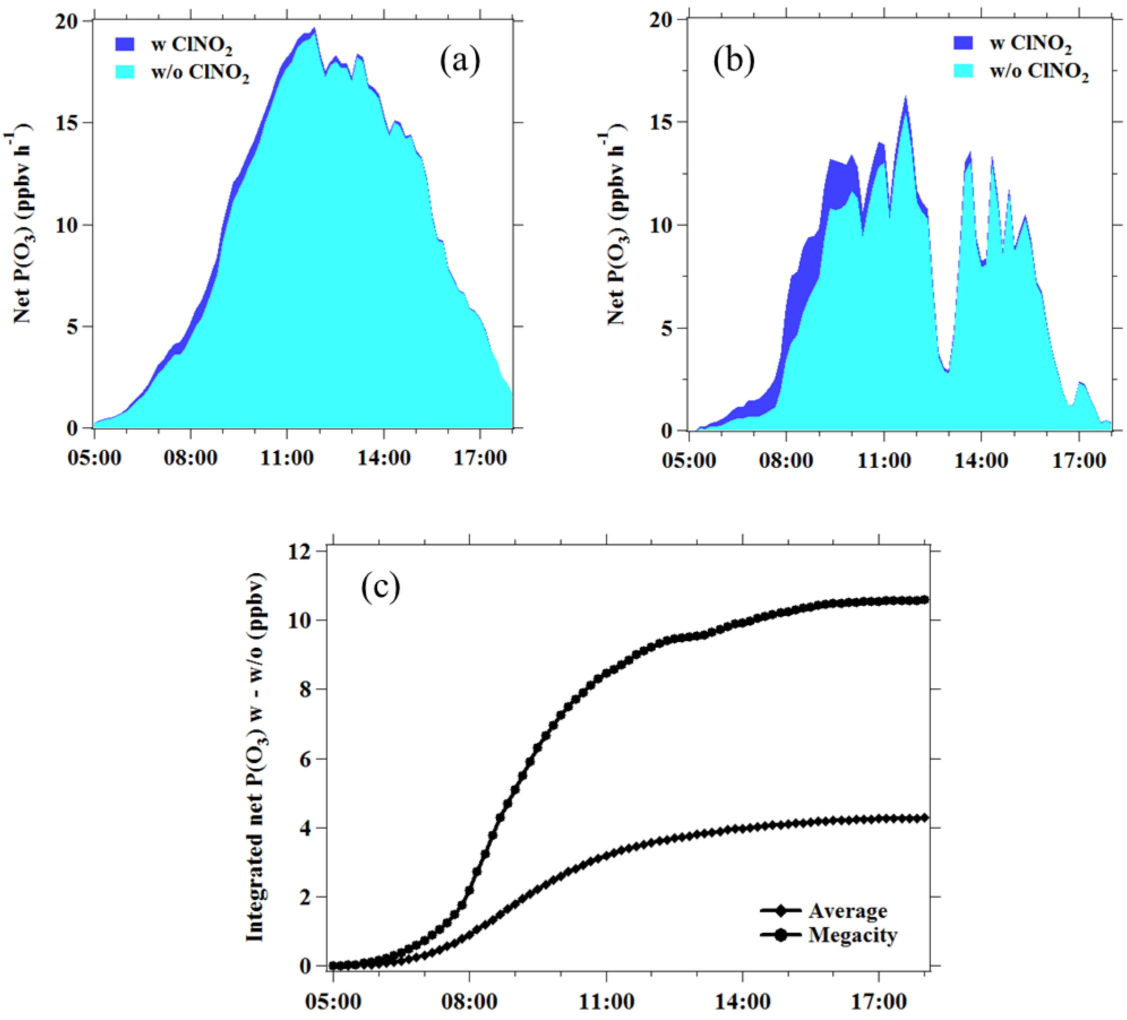


Figure 11. Net ozone production rates for a) average, b) the megacity case and c) the difference ~~of~~ in integrated net ozone production rate between the simulation with and without the ClNO$_2$ input.