Response to reviewer comments on "Integration of Airborne and Ground Observations of Nitryl Chloride in the Seoul Metropolitan Area and the Implications on Regional Oxidation Capacity During KORUS-AQ 2016"

We would like to thank the reviewers for their careful consideration of the paper. The comments have been addressed and additional information has been added in the paper for clarification. The comments from the reviewers are in *black*, our responses are in *blue*, and parts that have been added to the manuscript are in ***bold blue***.

Reviewer #1

Jeong and co-authors present an analysis of ClNO2 observations from the 2016 NASA KORUS-AQ campaign. ClNO2, additional trace gases, and measurement of aerosol composition were collected aboard the NASA DC-8 aircraft as well as at two ground-based sites, which were the main focus of this study. The first site was located in the Seoul metropolitan area, while the second was located ~26 km southeast in a forested area. The same observation method was used for all ClNO2 measurements, allowing for direct comparisons between sites. Ground-based observations revealed that ClNO2 was elevated at night at both sites, with higher concentrations at the TRF forested site, which was physically removed from NO emissions, which reduce O3 concentrations and calculated nitrate radical production rates. At both sites, there were periods where ClNO2 persisted at high levels throughout the morning after sunrise. Using additional box-model simulations, the authors found that morning entrainment of ClNO2 from the residual layer, nor morning ClNO2 production could reconcile differences between the simulations and observations. Based on these results and backward air mass trajectories, the authors conclude that horizontal transport is the likely cause of elevated morning ClNO2 concentrations. A final set of 24-hour simulations with and without ClNO2 production, constrained to observations, revealed that chlorine radical initiated chemistry can increase net O3 production in the morning by between 2 and 25%.

The authors have provided a succinct and novel analysis that merits publication after the following comments are addressed. First, this manuscript requires more details in the methods section about the box model set-up and the types of simulations that were conducted. Specific comments are provided below. Without additional details, it is difficult to fully assess the model results presented here. Second, the authors conclude that horizontal transport is the most likely cause of elevated surface-level morning ClNO2, without providing sufficient evidence. The authors present three possible causes based on previous studies and find no evidence for the first two, and therefore conclude that the third, transport, must be the main source. While this may be the actual cause, the authors need to provide additional evidence for this conclusion as discussed in specific comments below. Other comments largely include additional suggested references, requested clarification of the calculated net O3 and NO3 radical production rates and aerosol surface area, and other minor and editorial comments.

Major Comments:

Instrument Section:

Ln 130 – The authors note that ClNO2 is thermally converted to NO at 325 C in a CL instrument. The thermal conversion efficiency of ClNO2, however, is estimated to be between 300 – 500 C, depending on the inlet and heater set-up and flow rate of a particular instrument (e.g. Thaler et al., 2011; Wild et al., 2014; Wooldridge et al., 2010). As the CL instrument was used to calibrate the CIMS ClNO2 measurement, the authors should discuss how they accounted for (or quantified) the thermal conversion efficiency of ClNO2.

The following has been added for clarity:

> (Ln 147-149) **"$ClNO_2$ is detected as NO_y in the CL through conversion to NO on the heated (325 °C) molybdenum catalytic converter (Williams et al., 1998). The efficiency of the conversion was assumed to be unity."**

Model Description Section:

More details are required in this section about the model set-up and the types of simulations that were conducted.

Ln 135 –State which meteorological parameters were used as constraints. Also clarify the type of simulations that were run and how the model was constrained with observations. For example, were simulations run for 24, 48, 76 hours? Were simulations constrained every 10 minutes, 1 hours, 6 hours, etc.? Were different simulations run and constrained to observations from both of the ground sites or was a single simulation run with a combination of the two?

The 2.3 Modeling section was revised as suggested:

> (Ln 155-156) **"Each step of the model was constrained with the averaged meteorology parameters (e.g., pressure, temperature, relative humidity) and trace gases observed…"**

Additional information of the model setup has been included in the supplementary:

> (Supplementary Ln 31-34) **"Daytime steady state Cl_2 simulations (Figure 5) were constrained with meteorology and trace gas observations corresponding to each point of the data shown in Figure 4. The constrained parameters were kept constant throughout the 72 hours of integration time and the end points are shown in Figure 5. Steady state simulations of $ClNO_2$ production in the morning (Figure 8) were ran similarly by holding constant of all the measured parameters throughout the runs, except for $ClNO_2$."**

> (Supplementary Ln 49-55) **"Impact of measured $ClNO_2$ on O_3 production (Figure 10) was explored by constraining the box model with diurnal variation of observations throughout each step. Constraining the model with the diurnal variation of measured $ClNO_2$, allowed the box model to capture its trend throughout the course of the day.**

> **Since our purpose of the simulations were to explore the possible impact of $ClNO_2$ on O_3 production, NO_2 and O_3 were only constrained initially at the first step with observations and then calculated based on the chemistry embedded in the model. More specifically, the initial concentration of each following step was taken from the value in the previous step. The integration time in the model was 100 sec and the model was run for 1 day.”**

Ln 149 – Clarify, did the authors apply a hygroscopic growth factor to the measured aerosol surface area? What was the size range of the aerosol particles that contributed to the measured surface area? Did aircraft vertical profiles show that the aerosol surface area was relatively constant with altitude? As there are no measurements of aerosol surface area on the ground, this source of uncertainty in the model should be discussed. In addition, it would be helpful to put the N2O5 uptake coefficient into context. The authors could cite previous studies that derived uptake coefficients in Asia (e.g. Brown et al., 2016; Tham et al., 2016; Wang, Z. et al., 2017; Wang, X. et al., 2017; Wang, H. et al., 2017). As this manuscript is primarily about ClNO2 production, the authors should also state how the ClNO2 yield was calculated in the model. In the event that the Bertram and Thornton parameterization was used, it is also important to note that this has been shown to be an over- prediction of field-derived yields (McDuffie et al., 2018a; Riedel et al., 2013; Ryder et al., 2015; Tham et al., 2018; Thornton et al., 2010; Wagner et al., 2013; Wang, Z. et al., 2017; Wang, X. et al., 2017).

The following has been added in the supplementary for clarity:

> (Supplementary Ln 34 - 48) “**Heterogeneous reactions of gas-phase N_2O_5 (i.e., $N_2O_{5(g)} + Cl^-_{(aq)} \rightarrow ClNO_{2(g)}$), $ClONO_2$ (i.e., $ClONO_{2(g)} + Cl^-_{(aq)} + H^+_{(aq)} \rightarrow Cl_{2(g)} + HNO_3$), and HOCl (i.e., $HOCl_{(g)} + Cl^-_{(aq)} + H^+_{(aq)} \rightarrow Cl_{2(g)} + H_2O$) were included in the model. For these heterogeneous reactions, a simple first-order reaction was assumed by accounting for γ, Φ, molecular speed of the gases, and surface area of aerosols. Hygroscopic growth factor was not considered in the model. γ_{N2O5} was calculated from the Bertram and Thornton (2009) study using measured inorganic aerosol composition, temperature, and relative humidity and water content derived from the thermodynamic model Extended Aerosol Inorganics Model (E-AIMS, (Clegg et al., 1998; Friese and Ebel, 2010)). The average and median γ_{N2O5} values during the whole campaign were both 0.017. This is in the lower range of what has been derived from previous field observations in Asia that ranges from a campaign average of 0.004 to 0.072 (Yun et al., 2018; Brown et al., 2016; Tham et al., 2016; Wang et al., 2017b, d, a, c). γ values of $ClONO_2$ and HOCl were set to 0.06 (Deiber et al., 2004; Hanson et al., 1994; Hanson and Ravishankara, 1994). The yields (Φ) of the three heterogeneous reactions were assumed to be 1, therefore the steady state simulations would be an upper-limit of Cl_2 or $ClNO_2$ production. Aerosol surface area was taken from airborne measurements of particle size distributions. An averaged value was used from data retrieved below 1 km over the SMA. The airborne data did not show a significant**

> **vertical dependence within the daytime boundary layer. Based on this, an average of 78 ± 41 $\mu m^2 cm^{-3}$ were estimated for particle sizes between 10 nm and 5 μm.”**

Ln 150 – Add more details about the FLEXPART simulations. For example, add more details such as those in the Figure 3 caption.

The following has been added for clarity:

> (Ln 173 - 180) **“The FLEXible PARTi-cle dispersion model (FLEXPART v9.1, https://www.flexpart.eu) was used for the air mass source contribution (Figure 3) and backward trajectory analysis (Figure 9). The backward trajectories reported in our study were initialized 9:00 LST at TRF, following it 24 hours back in time. The trajectories were driven by the National Centers for Environmental Prediction (NCEP) Global Forecast System (GFS) with a 0.25 degree resolution. Influence of air mass originating from the ocean at TRF and OP was calculated every 6 hours following an air mass 5 days back in time. Meteorology was driven by WRF with a 5 km horizontal resolution. Since emissions of CO are very low in the ocean, and assumed to be inert in the model, it was used as a tracer for contribution of air originating from the ocean within a given air mass at each ground site.”**

Results and Discussion Section:

Ln 161 – The statement that ClNO2 rapidly photolyzes near sunrise contradicts the authors later statements on line 213 that ClNO2 persists after sunrise.

Line 265 has been re-written as below:

> **“At both sites, $ClNO_2$ levels started to increase or sustained after the first 2-3 hours of rapid net loss upon sunrise.. ”**

Paragraph starting on line 243 –Is there further information in the flight data to support the hypothesis that boundary layer transport is the main source of elevated surface-level ClNO2? For example, were NOx and O3 observations to the west of the observation sites elevated relative to the east? My concern is that this section reads as though the third proposed possibility must be correct since there was no evidence for the first two possibilities. As written, there is not enough evidence in this section to support the third possibility that transport is the main source of surface-level ClNO2.

Following has been included in the discussion

> (Ln 299-305) **“During KORUS, the DC-8 did not fly to the west of the SMA in the early morning. However, there are large point sources, such as petrochemical facilities and industries, and vehicular emissions to the west and south west of the SMA region. Sullivan et al. (2019) reported that this resulted in enhanced levels of O_3 in**

receptor regions (i.e., Taehwa Research Forest) downwind when westerlies were prevalent. Therefore, favorable conditions such as high chloride content in aerosols from both anthropogenic and natural sources and high levels of NO_x-O_3 could have lead to significant levels of $ClNO_2$ to build up and transported to TRF before being completely photolyzed. During the campaign, influence of large biomass burning was negligible as reported in Tang et al. (2018, 2019).”

Section 3.3.

It is unclear how ClNO2 was used to constrain the model simulations. For example, was the model only initialized with observed ClNO2 mixing ratios, or was the model constrained to observations throughout the morning? As the authors spend time in the previous section discussing the elevated morning ClNO2, it seems important that model simulations emulate that observed behavior.

A more detailed description of the box model runs have been added in the methods and supplementary. The following has been added for clarity:

> (Supplementary Ln 49-51) **“Impact of measured $ClNO_2$ on O_3 production (Figure 10) was explored by constraining the box model with diurnal variation of observations throughout each step. Constraining the model with the diurnal variation of measured $ClNO_2$, allowed the box model to capture its trend throughout the course of the day”**

Conclusions:

The authors mention that stagnation events were associated with low ClNO2 production. There was no discussion in the text, however, about the meteorology associated with these low ClNO2 events. Moreover, past studies have shown that certain types of stagnation events can actually enhance N2O5 chemistry (e.g. Baasandorj et al., 2017).

Description on the meteorology during the campaign have been included in the Methods section for clarity:

> (Ln 110-115) **“Meteorology during the observation period can be classified into dynamic (May 4th - 16th), stagnation (May 17th - 22nd), transport (May 25th - 31st), and blocking period as shown in Figure 3. During the stagnant period, high pressure system was persistent in the Korean peninsula resulting in local air masses to be more dominant within the SMA compared to the dynamic and transport (May 25nd - 31st) periods. Rex block patterns were observed during the blocking period (June 1st - 6th), which also resulted in more local influence.”**

The following have been included in the discussion for further discussion on stagnation events and N_2O_5:

> (Ln 236 -241) **“Stagnation events can be characterized by low wind speeds and increased atmospheric stability, possibly leading to enhanced levels of pollutants like NO_x. Previous studies have shown that these stagnant conditions can result in enhanced levels of N_2O_5 (Baasandorj et al., 2017) driven by high ozone and NO_2.**

> **However, ClNO$_2$ production was limited during stagnation events in this study. This is likely due to limited availability of chloride as shown in submicron particle measurements of aerosol mass spectrometer (AMS) at the ground site for OP and airborne over TRF (Figure 3).”**

Minor Comments:

Throughout text – change ‘ppb’ to ‘ppbv’ and ‘ppt’ to ‘pptv’

Changes have been made throughout the text.

line (ln) 16 – The authors reference the laboratory work of Roberts et al. (2008) showing Cl2 production from N2O5 uptake on acidic, chloride-containing aerosol (R5). There is no known field evidence of this reaction occurring on ambient aerosol, even at low pH. For example, the recent study by McDuffie, E. E. et al. (2018) found a negative correlation between particle acidity and Cl2(g) during the WINTER aircraft campaign, which is the opposite expected trend from this reaction. While this one study cannot confirm or deny the presence of the net N2O5 → Cl2 reaction, the authors should note that there are uncertainties regarding the occurrence of this particular reaction on ambient aerosol.

The following has been added:

> (Ln 21) **“However, this reaction has yet to be proven in ambient conditions.”**

Ln 18 – In addition to the decreased lifetime of NO3 during the day, the short lifetime of N2O5 is largely due to its thermal instability during the day.

The sentence has been revised as below:

> (Ln22-23) **“During the day, N$_2$O$_5$ exists at low levels due to its thermal instability (Malko and Troe, 1982) and the short lifetime of NO$_3$ (NO$_3$ < 5 s) from photolysis and reaction with NO (Wayne et al., 1991).”**

Ln 19 – define ‘reactive chlorine’

The sentence has been revised as below:

> (Ln 23-24) **“Particulate Cl$^-$ and chlorine containing gas species can come from both natural sources such as sea salt…”**

Ln 35 – since there is discussion of the efficiency of ClNO2 production, it might be helpful to change R4 to the following reaction to show the dependence of ClNO2 on the ClNO2 yield and N2O5 uptake coefficient.

R4 has been replaced as below:

$$N_2O_{5(g)} \xrightarrow{\gamma(N_2O_5),Cl^-(aq)} (2-\phi)*HNO_{3(g)} + \phi*ClNO_{2(g)} \qquad \text{(R4)}$$

Paragraph starting on 37: There are many more observations than the few U.S. studies that are referenced. It is not necessary to cite all of these past studies, however, there are a growing number of observations in Asia, which should be referenced/discussed here as this is the focus area of this manuscript. Including, but not limited to: (Liu et al., 2017; Tham et al., 2018; Tham et al., 2016; Tham et al., 2014; Wang, X. et al., 2017; Wang et al., 2016; Wang, Z. et al., 2017; Wang et al., 2018; Wang et al., 2014; Yun, Hui et al., 2018). Many of these studies are discussed in the paragraph starting on line 66, but should still be referenced here when first discussing the history of ClNO2 measurements.

The sentences have been rearranged and further revised to include the studies in Asia.

> (Ln 55-64) **"More recently (in the past 5 years), increasing number of ClNO$_2$ observations have been conducted in Asia consistently showing significant levels of ClNO$_2$ present in the boundary layer (e.g., Tham et al. 2018, 2016; Wang et al. 2016, 2017c, 2014; Yun et al. 2018; Liu et al. 2017). ClNO$_2$ observations at semi-rural (Wangdu of Hebei province) and urban (Hong Kong, Jinan) regions in China have measured up to 2 ppbv and 776 pptv respectively. At the mountain top (957 m above sea level) in Hong Kong, up to 4.7 ppbv of ClNO$_2$ was reported. The high levels of ClNO$_2$ in these studies were mostly correlated with continental pollution in vicinity (e.g., power plant plumes, biomass burning). A recent study by Yun et al. (2018) reported the highest ClNO$_2$ (8.3 ppb), during a severe have event in a semi-rural site downwind of the Pearl River Delta in the winter. Overall, observations have shown that ClNO$_2$ is ubiquitous in the tropospheric boundary layer."**

Ln 57 – Add a reference for the model tendency to underestimate ClNO2. For instance, if the simulated ClNO2 yield is too large, an underestimation in emissions would not necessarily lead to an underestimation of ClNO2. The authors should additionally add a statement in this section about current uncertainties in the ClNO2 yield as this adds uncertainty to model-predicted ClNO2 as well. This topic was recently reviewed in McDuffie et al. (2018a) and references therein.

The sentences have been re-written as below :

> Ln 66-68 **"Uncertainties in model simulated ClNO$_2$ can arise from limited emission inventories, low resolution of the grid, uncertainties in γ_{N2O5} and Φ_{ClNO2} parameterization, complexity of the terrain, and meteorological conditions and these have been dealt in previous studies (e.g., Zhang et al. 2017; McDuffie et al. 2018b, a; Lowe et al. 2015; Sarwar et al. 2012, 2014; Sherwen et al. 2017)."**

Ln 66 – Add a citation to Yun, H. et al. (2018), who report the largest concentrations of ClNO2 to-date (8.3 ppbv!)

> (Ln 61-63) "**A recent study by Yun et al. (2018) reported the highest $ClNO_2$ (8.3 ppb), during a severe have event in a semi-rural site downwind of the Pearl River Delta in the winter.**"

Ln 85 – As this study also includes a box model analysis, the authors should include a reference to this part of the analysis here.

> (Ln 97) **"We present observational and box model results to evaluated the impact of ClNO2 towards regional air quality in SMA."**

Ln 100 – Were THS CIMS used at both ground sites and on the NASA DC-8? Please clarify. Much of the information in this paragraph could be moved to the SI since the iodide adduct chemistry with ClNO2 and Cl2 is not novel and has been used for many of the past measurements of these species.

We agree with the reviewer that the iodide adduct chemistry is not novel and has been used in many previous studies. However, the information included in our method section is just a very brief summary of it, which we believe will help the readers for better understanding.

The same THS quadrupole CIMS were used at both ground sites and also on the DC-8. The related sentences have been revised as below for clarity:

> (Ln 117-118) **"A THS Instruments LLC Chemical Ionization Mass Spectrometer (CIMS), using iodide (I^-) as the reagent ion was used for measuring Cl_2 and $ClNO_2$ at the two ground supersites and on the NASA DC-8."**

Ln 107 – It is unclear which CIMS instrument is being discussed here, or whether all three instruments have the same configuration. Please clarify.

We used the same CIMS system on the two ground sites and airborne. However, the inlet configuration slightly varied as described in the manuscript. For clarification, the sentence has been revised as below:

> (Ln 123-125) **"Therefore, the use of different types of inlets (e.g., the use of the donut), described above, at the two ground sites and on the DC-8 is not expected to be an issue for the quantitative comparisons in this study."**

Ln 161 – The authors use LST here and throughout the text and KST in Figures 2 and 3. Please change for consistency.

Changed

Ln 167 – Riedel et al. (2012) have also extensively discussed the correlation between Cl2 and ClNO2 in data offshore of LA, which should be cited/discussed here. It is helpful to discuss similarities and differences with additional urban areas outside of Asia.

Comparison with Riedel et al. (2012) has been included as below:

> (Ln 190-192) **“Nighttime relationship between $ClNO_2$ and Cl_2 varied day by day and did not show a clear correlation. This implies that the sources of Cl_2 and $ClNO_2$ was not consistent at night. This is similar to Riedel et al. (2012), where they reported a wide range of correlation between Cl_2 and $ClNO_2$ off the coast of LA ”**

Ln 172 – 175 – Please clarify here how the presence of power plants and aerosol organics would impact the observed ClNO2/Cl2 correlation.

Ln 174-176 have been removed and the following sentence has been re-written as below:

> (Ln 203-205) **“However, in this study, the $ClNO_2$ measured at both the OP and TRF sites was weakly correlated with SO_2 (R^2 = 0.02), which implies that the air masses that we sampled are not fresh emissions from power plants.”**

Ln 180 – As previously mentioned, it should also be noted here that there is currently no field-evidence for this reaction.

The following has been added:

> (Ln 210) “**Therefore, the efficiency of this reaction in ambient conditions requires further investigation.**”

Ln 200 – Please add details about the calculation of the nitrate radical production rate, such as the rate coefficient that was used. It is also unclear here how a ‘slow nitrate radical production rate’ is consistent with a rapid drop in ClNO2 at 22:00 LST.

The suggestions have been added as below:

> (Ln 251-253) **“The trend was consistent with slower nitrate radical production rate ($d[NO_3]/dt = [NO_2]*[O_3]*k$, where $k= 3.52\times10^{-17}$ at 298 K, Atkinson et al., (2004)), as O_3 was titrated to zero by NO close to midnight.”**

Ln 201 – At night the boundary layer becomes vertically stratified, which results in a surface layer and residual layer.

The sentence has been removed.

Ln 211 – There have been multiple studies that have discussed the change in N2O5 chemistry with altitude. Many of these have been in the context of nitrate aerosol production. It would be good to reference some of this past work (in addition to Brown et al. (2017)) when discussing the change in ClNO2 production with altitude. For example: (Baasandorj et al., 2017; Tham et al., 2016; Young et al., 2012; Yun, Hui et al., 2018)

The references have been added and discussed as below:

> (Ln 254-259) **"However, significant levels of N_2O_5 and $ClNO_2$ could have been present in the upper part of the surface layer as shown in previous studies (Baasandorj et al., 2017; Young et al., 2012; Yun et al., 2018). According to Baasandorj et al. (2017), significant levels of N_2O_5 were observed aloft, within the boundary layer, while O_3 was completely titrated near the surface. On the other hand, airborne measurements at the LA basin (Young et al., 2012) showed a relatively uniform $ClNO_2$ profile throughout the boundary layer as O_3 did not change significantly within the measured altitude."**

Ln 235 – Figure 9 does not show the agreement between the observed and simulated ClNO2 mixing ratios as indicated. The authors might have meant to reference Figure 7.

The reference to figure 9 has been corrected to 8 in the text.

Ln 257 – Please define net O3 production rate and explain how this was calculated from model simulations.

The following has been included in the supplementary for clarity:

> (supplementary Ln 55-57) **Net O_3 production rate was calculated in the box model as below, where f is the stoichiometric coefficient of O_3 and k is the rate constant corresponding to each reaction i. More details can be found in the supplements of Wolfe et al. (2016) :**
>
> $$d[O_3]/dt = O_3\ \text{production rate} - O_3\ \text{loss rate} = \sum_{i=1}^{\#\ of\ reactions} fi \times (product\ of\ reactants)i \times ki$$

Table 1 – Clarify that chloride, nitrate, and sulfate are concentrations from particles < 1um in diameter.

Changed

Figure 1 – Increase the text size and resolution of the images in panel a. The insert is difficult to read.

Changed

Figure 2. The NOx observations should be averaged to the same time interval (i.e., 10 minutes) to allow for direct comparison between the sites.

Changed

Figure 3 – This timeseries makes Cl2 appear as if it has a constant background of ~2 pptv at each site. Could the authors comment on this background and discuss whether it is real or an instrument artifact?

Figure 3 has been corrected to remove data points below detection limit. For Cl_2, the detection limit was around 2.9 ppt (2 sigma, over 30 min).

Figure 6 – Expand panel a to increase the visibility of the ClNO2 data.
Changed

Figure 7 – Clarify that sunrise is at time zero. Clarify what the standard deviations are referring to. The authors should also mention why ClNO2 at t=0 is 0 ppbv when there is actually ClNO2 present at sunrise.

Figure 8 caption has been revised as below:

> **"Steady state $ClNO_2$, simulated from a box model constrained with airborne measurements (blue) and ground site data from TRF (red), when there was morning $ClNO_2$ peak in the morning. Averaged values of the model runs are shown here with standard deviations."**

More details of the box model simulations were added as below:

> **(Supplementary Ln 31-34) "Daytime steady state Cl_2 simulations (Figure 5) were constrained with meteorology and trace gas observations corresponding to each point of the data shown in Figure 4. The constrained parameters were kept constant throughout the 72 hours of integration time and the end points are shown in Figure 5. Steady state simulations of $ClNO_2$ production in the morning (Figure 8) were ran similarly by holding constant of all the measured parameters throughout the runs, except for $ClNO_2$."**

SUPPLEMENT
Section 1 –
As the AMS typically reports aerosol pH, the authors should compare their pH calculations to those from the AMS.
The AMS doesn't typically report aerosol pH. The AMS does provide ammonium balance but previous studies (Hennigan et al., ACP, 2015; Guo et al., JGR, 2016; etc.) have shown that this solely can't be used to determine aerosol pH. This is due to aerosol pH having a non-linear relationship with temperature and liquid water/RH (e.g., Guo et al., JGR, 2016; Guo et al., ACP, 2017; Song et al., ACP, 2018). Similarly, subtracting anions from cations to get H^+ concentration wouldn't be plausible since H^+ depends on water and temperature. Therefore, the

only way to determine pH would be through running a thermodynamic model as have been done in our study.

Figure S1 – Clarify whether this inlet configuration is for the ground-based CIMS or aircraft instrument. If for the ground-based CIMS, was it the same for both instruments?

> (Supplementary Ln 5-8) **"During the KORUS-AQ 2016 field campaign a chemical ionization mass spectrometer (CIMS) was deployed to measure Cl_2 and $ClNO_2$. These systems were deployed at the Taehwa Research Forest (TRF), Olympic Park (OP), and on-board the NASA DC-8. The configuration of the inlet at the two ground sites is shown in Figure S1. The CIMS on the DC-8 had a similar configuration but without the heating inlet."**

Figure S6 – It is unclear how the May 5th profile of ClNO2 relates to the diurnal average profile. The font size of the insert also needs to be increased.

As mentioned in the Ln 270-271, in the morning of May 5th at TRF, maximum levels of $ClNO_2$ net production was required to reconcile the measurements. This insert was included as the 'max' case along with the 'average' case. The font size of the insert has been adjusted.

Editorial Comments:

Throughout the text – check the consistency of 'aerosol' vs. 'aerosols' when using the plural form

changed

line (ln) 5 – Change "in both sites" to "at both sites"

changed

ln 6 – Either change "variation" to "variations" or "were" to "was"

changed

ln 11 – Either change to "the net ozone production rate" or to "net ozone production rates by"

changed

ln 15 – Change to ", which generated from an equilibrium reaction with…"

changed

ln 16 – Change "In acidic aerosols" to "On acidic aerosol"

changed

ln 20 – Change to "coal-fired power plants"

changed

ln 22 – Change to "N2O5 aerosol uptake coefficient (g (N2O5)), aerosol surface area, and N2O5 mean molecular speed, as well as the yield…"

changed

ln 23 – The references provided are only a subset of the relevant literature. Change to (e.g., Thornton et al. …)

changed

In 29 – Change “level of ozone” to “ozone (O3) level”

changed

In 37 – change to “The first ambient measurements of ClNO2 were carried out by Osthoff et al. (2008), from a ship sampling along the southeastern U.S. coast in 2006”

changed

In 47 – change to “models”

changed

In 53 – Change 7 ppbv and 20% so that both O3 and OH changes are either reported in percent or ppbv.

Ln 78-79 has been changed as below:

“The results showed that, compared to the simulations without $ClNO_2$ formation, monthly 8 h wintertime maximum O_3 and □OH increased up to 15 % and 20 %, respectively.”

In 71 – Change “correlated to” to “correlated with”

changed

In 78 – Change from “observation results during” to “observations from”

changed

In 82 – Change “were conducted” to “were collected”

changed

In 83 – Change to “and included airborne observations from the NASA DC-8…”

changed

In 84 – Change “ground” to “ground-based”

changed

In 95 – Change to “research flights when ClNO2 was measured’.

changed

Ln 105 – Change to “in various field conditions”

changed

Ln 106 – Change to “at the two ground sites”

changed

Ln 110 – Define slpm

revised

Ln 111 – PTFE is used on line 103, prior to the definition here.

Revised to define earlier

Ln 157 – Change to “During most nights…”

changed

Ln 161 – Change to “At both sites,…”

changed

Ln 164 – Change to “positive correlation with Cl2…”

changed

Ln 173 – Change to “the ClNO2 measured at both the OP and TRF sites was weakly correlated…”

changed

Ln 175 – Add “e.g.,” before the McDuffie et al. (2018b) and Thornton et al. (2003) references as there have been many more studies that have looked at the organic influence on N2O5 uptake.

changed

Ln 184 – Change to “at the ground sites was highly correlated with the origin of the air mass…”

changed

Ln 185 – Change to “During the nights shaded in red in Figure 3 …”

changed

Ln 186 – Change to “there was limited production of ClNO2 at the surface.” Also, change to “These periods corresponded to low contributions from air masses originating over the ocean and with limited particle chloride concentrations measured by the…”

changed

Ln 190 – Change to “when nitrate production was limited at the surface due to O3 reaction with NO, ClNO2…”

changed

Ln 198 – Change to “significant levels of ClNO2 were sustained throughout the night during most of the…”

changed

Ln 204 – Change to “near the surface”

changed

Ln 207 – Change to “a Cavity Ringdown Spectrometer (CRDS) was installed on top of the Seoul tower in May -June that measured N2O5, NOx, and O3”

changed

Ln 209 – Change to “the average nighttime O3 mixing ratio was around 50 ppbv and N2O5 was observed most nights, with mixing ratios reaching up to 5 ppbv.”

changed

Ln 226 – Change to “At night…”

changed

Ln 233 – Change to “However, the remaining flights observed an average of only 17 ± 56 pptv of ClNO2 (black circles).”

changed

Ln 255 – Change to “methods section.”

changed

Ln 270 – Place the reference to Tham and Wang in parentheses.

changed

Figure 3 - Remove the extra ‘)’ after m-3. Change to “ClNO2 and Cl2 observations and results…”

changed

Figure 5 – Change to “Diurnal variation of ClNO2 and other parameters and trace gases calculated and measured during the campaign…”

changed

Figure 9 – provide a label for the x-axis.

changed

SUPPLEMENT

Ln 5 – Change to “model was run in the reverse mode”

changed

Ln 16 – Change to “model was run similarly here, and it took…”

changed

Ln 21 – Change to “pH and liquid water concentrations for sub-micron aerosol.”

changed

Figure S5. Change to “production rate of the nitrate radical.”

changed

Figure S6 – Change to “The insert in (b) is the…”

changed

Figure S7 – Change the Figure 5 reference to Figure 6.

changed

Reviewer #2

Jeong et al. reported ground-based and airborne observations of ClNO2 in Korea during the Korean- United States-Air Quality (KORUS-AQ) 2016 field campaign. They analyzed the general characteristics, the sources and the effects of ClNO2 on ozone during their measurement campaign. The study contributes to the growing body of ClNO2 measurements around the world, and the content fits the scope of *Atmospheric chemistry and Physics.* The manuscript can be improved by adding more detailed description of measurements and more in-depth analysis/discussion on the elevated levels of ClNO2 in the morning. In addition, there are a number of places which need to be modified for clarity.

Specific comments

(1) Introduction: the manuscript gave a detailed review of measurements of ClNO2 conducted in North America and Europe, but didn’t include some recent work in Asia (mostly in China). As the latter is more relevant to the present study due to proximity of the study regions, these studies should be reviewed (following the review of North America/Europe results). These studies are listed below:

· Wang, H., Lu, K., Guo, S., Wu, Z., Shang, D., Tan, Z., Wang, Y., Breton, M. L., Lou, S., and Tang, M.: Efficient N2O5 uptake and NO3 oxidation in the outflow of urban Beijing, Atmospheric Chemistry and Physics, 18, 9705-9721, 2018.

· Zhou, W., Zhao, J., Ouyang, B., Mehra, A., Xu, W., Wang, Y., Bannan, T. J., Worrall, S. D., Priestley, M., and Bacak, A.: Production of N2O5 and ClNO2 in summer in urban Beijing, China, Atmospheric Chemistry and Physics, 18, 11581-11597, 2018.

· Yun, H., Wang, W., Wang, T., Xia, M., Yu, C., Wang, Z., Poon, S. C. N., Yue, D., and Zhou, Y.: Nitrate formation from heterogeneous uptake of dinitrogen pentoxide during a severe winter haze in southern China, Atmospheric Chemistry and Physics, 2018, 23, 10.5194/acp-2018-698, 2018.
· Wang, Z., Wang, W., Tham, Y. J., Li, Q., Wang, H., Wen, L., Wang, X., and Wang, T.: Fast heterogeneous N2O5 uptake and ClNO2 production in power plant and industrial plumes observed in the nocturnal residual layer over the North China Plain, Atmospheric Chemistry and Physics, 17, 12361-12378, 2017.

· X. Wang, H. Wang, L. Xue, T. Wang, L. Wang, R. Gu, W. Wang, Y. J. Tham, Z. Wang, L. Yang, J. Chen and W. Wang, Observations of N2O5 and ClNO2 at a polluted urban surface site in North China: High N2O5 uptake coefficients and low ClNO2 product yields, Atmospheric Environment, 156. 125-134. 2017.

More studies in Asia have been added as suggested:

> (Ln 55-64) **"More recently (in the past 5 years), increasing number of ClNO$_2$ observations have been conducted in Asia consistently showing significant levels of ClNO$_2$ present in the boundary layer (e.g., Tham et al. 2018, 2016; Wang et al. 2016, 2017c, 2014; Yun et al. 2018; Liu et al. 2017). ClNO$_2$ observations at semi-rural (Wangdu of Hebei province) and urban (Hong Kong, Jinan) regions in China have measured up to 2 ppbv and 776 pptv respectively. At the mountain top (957 m above sea level) in Hong Kong, up to 4.7 ppbv of ClNO$_2$ was reported. The high levels of ClNO$_2$ in these studies were mostly correlated with continental pollution in vicinity (e.g., power plant plumes, biomass burning). A recent study by Yun et al. (2018) reported the highest ClNO$_2$ (8.3 ppb), during a severe have event in a semi-rural site downwind of the Pearl River Delta in the winter. Overall, observations have shown that ClNO$_2$ is ubiquitous in the tropospheric boundary layer."**

(2) Line 14: The lifetime of ClNO2 depends on the photolysis rate which varies among regions, seasons, weather conditions, etc. It's better to specify the condition in which the lifetime of ClNO2 is ~ 30 min and provide a reference.

The suggested information has been added as below:

> (Ln 15-17) **"Nitryl chloride (ClNO$_2$) is a night time radical reservoir that generates chlorine radicals (Cl□) upon sunrise (R1), with a lifetime (τ_{ClNO2}) of ~ 30 minutes at midday in the northern hemisphere mid-latitude summer, under clear sky conditions (J_{ClNO2}=5.47×10^{-04} s^{-1}, (Madronich and Flocke, 1998))."**

(3) Line 17: "resulting from an enhanced ClNO2 uptake coefficient of up to 3 orders of magnitude" is not clear. Is the uptake in the condition of pH<2 "3 orders of magnitude" higher than that in the condition of pH=7? Please elaborate.

> (Ln 19-21) **“In acidic aerosols (~pH 1.8), uptake of N_2O_5(g) can also produce gas-phase chlorine (Cl_2, R5), resulting from enhanced $ClNO_2$ uptake coefficient of up to 3 - 4 orders of magnitude higher than neutral pH (Roberts et al., 2008).”**

(4) Line 21: on source of chloride, Fu et al. (2018） presents a fine chloride emission inventory for China. This can be a good reference here.

· Fu, X., Wang, T., Wang, S., Zhang, L., Cai, S., Xing, J., and Hao, J.: Anthropogenic Emissions of Hydrogen Chloride and Fine Particulate Chloride in China, Environmental Science & Technology, 52, 1644-1654, 2018.

The suggested reference has been added in Ln 26.

(5) Line 25: Is the heterogeneous uptake of ClNO2 on acidic particle (Roberts et al., 2008) taken into account in the calculation of the lifetime (30h) during the nighttime?

No, it was not taken into account since this specific reaction on enhanced uptake coefficient of $ClNO_2$ on acidic particles has been reported in a laboratory study by Roberts et al. (2008) and uncertainties do remain in terms of its efficiency in ambient aerosols.

(6) Line 45: These previous studies showed that ClNO2 is ubiquitous at surface, within the boundary layer or in the lower troposphere around the world. No evidence has shown that the ClNO2 is ubiquitous in the troposphere which could reach >10 Km above the sea level in mid-latitude region.

Re-written as below:

> (Ln 63) “**Overall, observations have shown that $ClNO_2$ is ubiquitous in the tropospheric boundary layer.**”

(7) Line 55-57: another modeling study Li et al. (2017) assessed the ozone impact of ClNO2 in East Asia including Korea.

· Zhang, L., Li, Q., Wang, T., Ahmadov, R., Zhang, Q., Li, M., and Lv, M.: Combined impacts of nitrous acid and nitryl chloride on lower-tropospheric ozone: new module development in WRF-Chem and application to China, Atmospheric Chemistry and Physics, 17, 9733-9750,2017.

The reference has been added as below:

> (Ln 84-85) **“Another modeling study of WRF-CHEM embedded with an updated chlorine chemistry, simulated 3-6 % of surface O_3 increase in the North China Plain and Yangtze River Delta during the summer (Zhang et al., 2017).”**

(8) Line 58-65: the discussion on model resolution does not seem to be relevant to the present study.

The discussion on model resolution was included to present the discrepancies remaining between observation and model results. These discrepancies lead to the importance of more observations being required in different chemical regimes.

(9) Line 64-65: I assume that the authors are referring to the simulations by Sherwen et al. (2017) that underestimated the ClNO2 by 7 times. Please confirm.

The reference has been added in the text as below:

> (Ln 73-74) **“Compared to observations, the simulations underestimated the $ClNO_2$ maxima levels by ~ 7 times in inland areas (Sherwen et al., 2017).”**

(10) Line 73-78 discusses importance of chorine source in coastal cities and gives the reader an impression that it is only important near coast. But measurement data have shown it is present far inland as shown in Thronton et al. (2010). A recent compilation of PM2.5 data also shows high levels of chloride are present in inland regions of China (Yang et al., STOTEN, 2017). The relevant sentence should be modified.

· Yang, X., Wang, T., Xia, M., Gao, X., Li, Q., Zhang, N., Gao, Y., Lee, S., Wang, X., and Xue, L.: Abundance and origin of fine particulate chloride in continental China, Science of The Total Environment, 624, 1041-1051,2018.

As mentioned in Ln 52 (“Recent studies show that high levels of $ClNO_2$ are also present in mid-continental regions.”) and in the following sentences, we give examples of field observations affected by continental pollution.

(11) Section 2.1. It would help to include a brief description of the meteorology during the campaign.

The following has been added as suggested:

> (Ln 110-115) **“Meteorology during the observation period can be classified into dynamic (May 4th - 16th), stagnation (May 17th - 22nd), transport (May 25th - 31st), and blocking period as shown in Figure 3. During the stagnant period, high pressure system was persistent in the Korean peninsula resulting in local air masses to be more dominant within the SMA compared to the dynamic and transport (May 25nd - 31st) periods. Rex block patterns were observed during the blocking period (June 1st - 6th), which also resulted in more local influence.”**

(12) Section 2.2 on CIMS and calibration: more detailed information is needed. What is the length of the sample line? Was it washed or replaced regularly in order to reduce the loss of N2O5? How frequent was the calibration? Was change of CIMS sensitivity to relative humidity taken into account in data reduction, and how? Could measurement of Cl2 with a Q-CIMS subject to interference? In line 115, 'the natural abundance of Cl2 and ClNO2 isotopes are approximately 9:6:1", what do the authors mean by this statement? No figure was shown and it is not clear how the isotopic ratios behave.

The sampling lines were cleaned regularly and $ClNO_2$ calibration was carried out before and after the campaign and with additional calibrations during the campaign for Cl_2. N_2O_5 data are not presented in this study. The sensitivity of the CIMS was taken into account by normalizing the signals to the water cluster (amu 147 I□$H_2{}^{18}O$). In the manuscript, it says "The natural abundance of Cl_2 and $ClNO_2$ isotopes are approximately 9:6:1 and 3:1 respectively." which means natural Cl_2 has an isotopic ratio of 9:6:1 and $ClNO_2$ has 3:1. The I□$^{37}Cl^{37}Cl$ (amu 201) was subject to interference with elevated signals that didn't match the isotopic ratio, therefore wasn't considered in our Cl_2 data.

(13) Line 131: How was HONO measured?

HONO is measured as NO_y with the chemiluminescence instrument (Thermo scientific 42i). This is done by conversion of HONO to NO on the oxidized molybdenum surface. The generation of $ClNO_2$ was monitored for a couple of days to ensure minimum production of HONO (Thaler et al., 2011). The data that showed a stable signal of $ClNO_2$ after 2-3 days of the experiment were considered in the calibration.

(14) Section 2.3. Add description on the calculation of the impact of ClNO2 on O3 production rate and on the running of FLEXPART model.

The following has been added in the supplementary:

> (supplementary Ln 55-57) **Net O_3 production rate was calculated in the box model as below, where f is the stoichiometric coefficient of O_3 and k is the rate constant corresponding to each reaction i. More details can be found in the supplements of Wolfe et al. (2016) :**
>
> $$d[O_3]/dt = O_3 \text{ production rate} - O_3 \text{ loss rate} = \sum_{i=1}^{\#\ of\ reactions} fi \times (product\ of\ reactants)i \times ki$$

The following has been added:

> (Ln 173 - 180) **"The FLEXible PARTi-cle dispersion model (FLEXPART v9.1, https://www.flexpart.eu) was used for the air mass source contribution (Figure 3) and backward trajectory analysis (Figure 9). The backward trajectories reported in our**

study were initialized 9:00 LST at TRF, following it 24 hours back in time. The trajectories were driven by the National Centers for Environmental Prediction (NCEP) Global Forecast System (GFS) with a 0.25 degree resolution. Influence of air mass originating from the ocean at TRF and OP was calculated every 6 hours following an air mass 5 days back in time. Meteorology was driven by WRF with a 5 km horizontal resolution. Since emissions of CO are very low in the ocean, and assumed to be inert in the model, it was used as a tracer for contribution of air originating from the ocean within a given air mass at each ground site."

(15) Line 136. Why is NO2 not constrained in the box model?

(Supplementary Ln 49-54) **"Impact of measured $ClNO_2$ on O_3 production (Figure 10) was explored by constraining the box model with diurnal variation of observations throughout each step. Constraining the model with the diurnal variation of measured $ClNO_2$, allowed the box model to capture its trend throughout the course of the day. Since our purpose of the simulations were to explore the possible impact of $ClNO_2$ on O_3 production, NO_2 and O_3 were only constrained initially at the first step with observations and then calculated based on the chemistry embedded in the model. More specifically, the initial concentration of each following step was taken from the value in the previous step.."**

(16) Line 138-139: elaborate how photolysis rates are determined by scaling on-board DC-8 measurements.

(Ln 158 - 166) "**Photolysis rate constants were derived through the hybrid method (Wolfe et al., 2016) in the F0AM box model. This method uses clear sky solar spectra from the tropospheric ultraviolet and visible radiation model (TUV v 5.2) and cross sections and quantum yields suggested by IUPAC. To capture the effects of pollution on photolysis rates, the ratio of the measured J_{NO2} to the F0AM modeled J_{NO2} was calculated. This ratio was then applied to other photolysis rate constants calculated in the model. Measured J_{NO2} was taken from the DC-8 actinic flux measurements (Charged-coupled device Actinic Flux Spectroradiometer; CAFS) when flying near SMA at altitudes under 1 km. A diurnal cycle was applied to the DC-8 measurement to determine j-values at other times of day. Photolysis rate constants of $ClNO_2$, Cl_2, and $ClONO_2$ were not present in the F0AM model and therefore taken directly from the DC-8 measurements."**

(17) Line 142-145. Please include the reactions and their rates in the paper, at least in the supplement.

The following sentences have been revised to add related references and sources of the reactions embedded in the model:

> (Ln 166-173) **"The Master Chemical Mechanism v3.3.1 (MCM) was taken from http://mcm.leeds.ac.uk/MCM and embedded in the box model. MCM v3.3.1 has a detailed gas photochemistry (i.e., 5832 species and 17224 reactions), including the oxidation of CH_4 and 142 non-methane primary emitted VOCs (Jenkin et al., 2015). Since MCM v3.3.1 only includes Cl· reactions with alkane species, additional chlorine chemistry was embedded in the model, similar to what Riedel et al. (2014) reported. This was done by including multiple Cl· precursors (e.g., Cl_2, $ClNO_2$, HCl, $ClONO_2$, HOCl) and Cl· reactions with non-alkane VOCs, such as alkene, alcohol, aromatics, alkynes, ketones, organic acids and nitrates. All the reactions embedded in the model can be found in the supplementary of Riedel et al. (2014) and Wolfe et al. (2016)."**

(18) Line 145-148: B&T (2009) parameterization is likely to overestimate N2O5 uptake coefficient. Also, did you assume ClNO2 yield to be unity?

The purpose of the box model simulation of $ClNO_2$ was to explore whether the runs can reproduce the levels that we observed in the morning. Based on the simulations, the model highly underestimated the measured levels by more than 60 times. Therefore, an overestimation of the N_2O_5 uptake coefficient or the yield of $ClNO_2$ would not change our conclusion.

The following has been added in the supplementary:

> (Ln 44-45) **"The yields (*Φ*) of the three heterogeneous reactions were assumed to be 1, therefore the steady state simulations would be an upper-limit of Cl_2 or $ClNO_2$ production."**

(19) Section 3.1. It would be interesting to see a comparison of the observed values in this study with those reported elsewhere.

$ClNO_2$ observations from previous studies have been dealt in the introduction.

(20) Line 164-165 and Line 176-181: If I understand correctly, (1) when O3 is low, Cl2 level is low but ClNO2 could be high or low, so ClNO2 does not have correlation with Cl2: (2) when O3 is elevated, ClNO2 has a good correlation with Cl2, which could be due to ClNO2 uptake on acidic aerosol to form Cl2 (Roberts et al., 2008). Then what would be the cause of the (1) situation? Why there is no production of Cl2 from ClNO2 uptake when O3 is low, considering that the uptake of ClNO2 on aerosol does not require the presence of O3? Is the pH not low enough? If the Cl2 is solely produced from the ClNO2 uptake, the correlation between ClNO2 and Cl2 at night should be good as well. Is it possible that the Cl2 is mainly formed by gas phase reactions which are initiated by the photolysis of ClNO2 and the reaction of HCl+OH, both of which requires the presence of light? I would recommend the authors to apply box model sensitivity studies to understand the characteristics of ClNO2 (and Cl2).

Box model analysis on the daytime Cl_2 production has been added in the study as below:

(Ln 210 - 230) **“Another possibility is the autocatalytic production of Cl_2 from heterogeneous reactions of gas-phase $ClONO_2$ (i.e., $ClONO_{2(g)} + Cl^-_{(aq)} + H^+_{(aq)} \rightarrow Cl_{2(g)} + HNO_3$, (Gebel and Finlayson-Pitts, 2001; Deiber et al., 2004)) and HOCl (i.e., $HOCl_{(g)} + Cl^-_{(aq)} + H^+_{(aq)} \rightarrow Cl_{2(g)} + H_2O$, (Vogt et al., 1996)) on particles. These reactions are also favored as particle acidity increases. In order to further investigate its possibility, daytime Cl_2 was simulated by constraining the box model with measurements of $ClNO_2$ and other trace gases corresponding to each data point in Figure 4. Based on the availability of parameters, we were able to simulate 1680 and 1229 runs for the OP and TRF, respectively. This corresponds to more than 96 % of the daytime data points shown in Figure 4. $ClONO_2$ and HOCl were set to 0.06 (Deiber et al., 2004; Hanson et al., 1994; Hanson and Ravishankara, 1994), which is an upper-limit of previous laboratory studies, and the yields were assumed to be unity. HCl generation from hydrogen abstraction of VOCs by Cl□ were included in the mechanisms used in the model runs. The end points of the 72 hour simulation results are presented in Figure 5. As shown in the Figure, the box model simulations were able to reproduce the positive correlation between Cl_2 and $ClNO_2$. Moreover, modeled Cl_2 was suppressed in low O_3 conditions, which corresponds to the observations. This can be explained by Cl□ reacting with O_3, producing ClO□, leading to gas-phase $ClONO_2$ and HOCl. These can react on acidic aerosols to generate Cl_2. Sources of Cl□ could be from photo-labile gas-phase chlorine compounds (e.g., Cl_2, $ClNO_2$, $ClONO_2$, HOCl) or oxidation of gas-phase HCl by OH. Although the reaction between HCl and OH is relative slow ($k = 7.86 \times 10^{-13}$ cm^3 $molecule^{-1}s^{-1}$ at 298K, (Atkinson et al., 2007)), it has been reported to be a significant source of Cl in the daytime (Riedel et al., 2012). A sensitivity test was carried out by comparing modeled Cl_2 between runs with and without HCl production from oxidation of VOCs by Cl□ (Figure S4 c,d). The results show that production of Cl_2 was suppressed by 40 - 70 % when HCl was not generated in the model. This significant contribution of gas-phase HCl as a Cl source, should be an upper-limit as the deposition of HCl was not considered in the model. Nonetheless, our analysis leads us to conclude that the mechanisms we have explored could be the main contributions of the daytime Cl_2 production during KORUS-AQ.”**

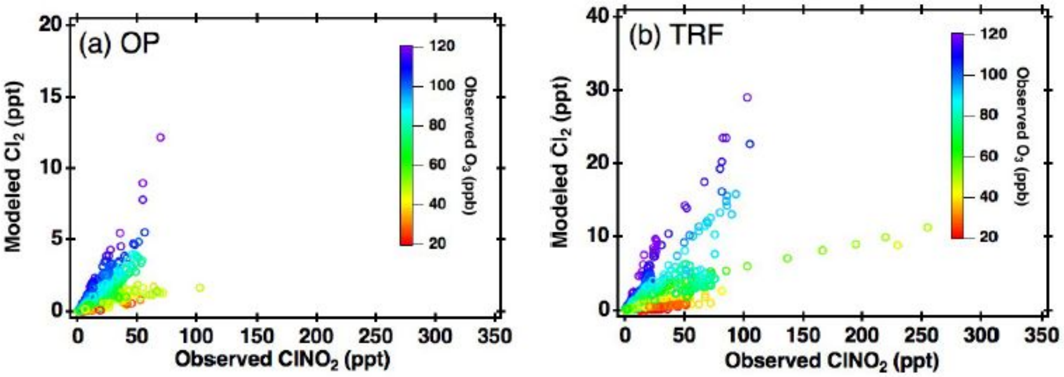

Figure 5. Correlation between box model simulated daytime (11:00 - 18:00 local time) Cl_2 and measured $ClNO_2$ at (a) OP and (b)TRF, color coded with measured O_3.

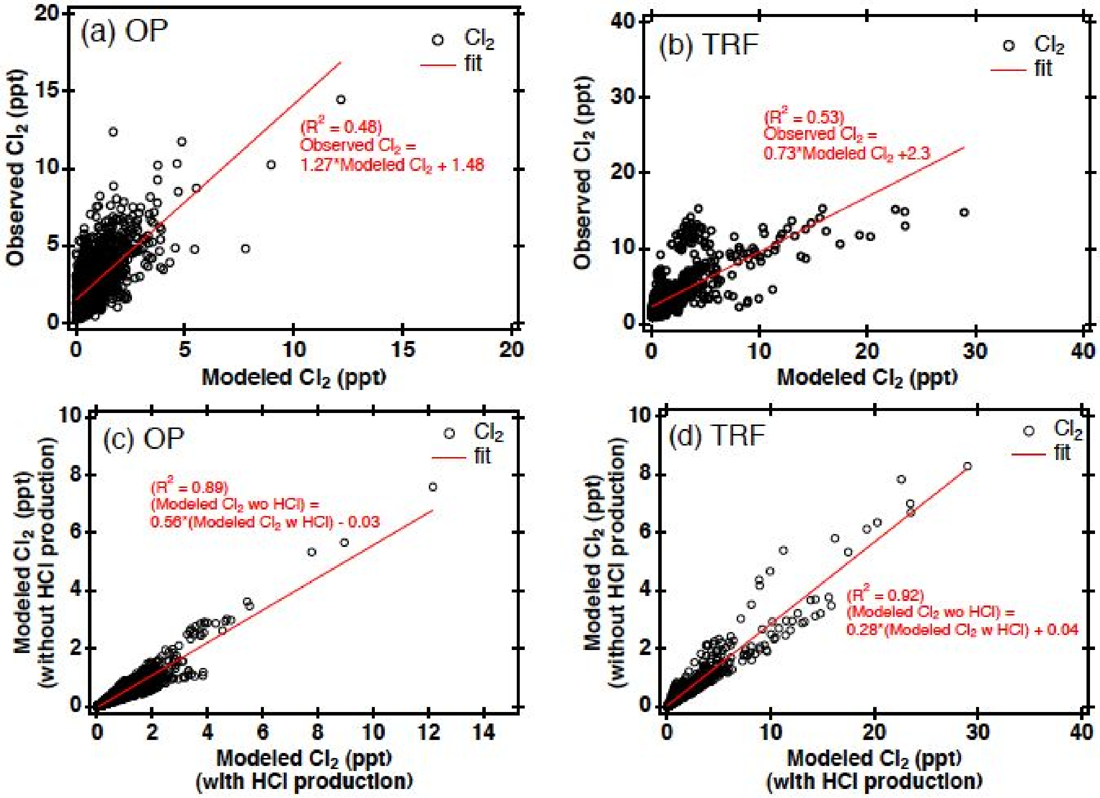

Figure S4. Correlation between measured Cl_2 and modeled Cl_2 at (a) OP and (b) TRF. Sensitivity tests of HCl were carried out (c and d) by switching off HCl production from chlorine radicals reacting with VOCs.

(21) Line 174-176: I don't see why the effect of organic coating on N2O5 uptake is relevant to the correlation of ClNO2 and Cl2.

Ln 174-176 have been removed

(22) Line 184-185: An explanation is needed for the calculation of ‘source contribution of CO’ using FLEXPART.

The following has been added for clarity:

> (Ln 173 - 180) **“The FLEXible PARTi-cle dispersion model (FLEXPART v9.1, https://www.flexpart.eu) was used for the air mass source contribution (Figure 3) and backward trajectory analysis (Figure 9)..... Influence of air mass originating from the ocean at TRF and OP was calculated every 6 hours following an air mass 5 days back in time. Meteorology was driven by WRF with a 5 km horizontal resolution. Since emissions of CO are very low in the ocean, and assumed to be inert in the model, it was used as a tracer for contribution of air originating from the ocean within a given air mass at each ground site.”**

(23) Line 184-185: Do the authors mean that the ClNO2 is highly correlated to the oceanic sources?Please elaborate.

> (Ln 241 - 242) **“Whether the chloride is from the ocean or anthropogenic emissions is uncertain since large point sources, such as power plants or petrochemical facilities, are also present along the west coast of the SMA”**

(24) Line 188-189: Apart from the back trajectory analysis, there are other methods to determine/estimate the source of chloride. Please refer to the previous studies on ClNO2 measurements. For example, In Line 172-174, the correlation of ClNO2 and SO2 is extremely low, so the coal-burning activity is not responsible for the chloride measured during the campaign. Any evidence of biomass burning, chemical signature (e.g. K+) or the fire detected by the satellite? Any evidence of sea-salt aerosol, e.g. how is the correlation of chloride and sodium? What about waste burning?

At the Taehwa Research Forest, there were no aerosol composition measurements carried out during the campaign. FLEXPART back trajectory analysis initialized at 9:00 LST shows an overall westerlies when there was a second morning peak of $ClNO_2$. The following has been added in the discussion:

> (Ln 299-305) **“During KORUS, the DC-8 did not fly to the west of the SMA in the early morning. However, there are large point sources, such as petrochemical facilities and industries, and vehicular emissions to the west and south west of the SMA region. Sullivan et al. (2019) reported that this resulted in enhanced levels of O_3 in receptor regions (i.e., Taehwa Research Forest) downwind when westerlies were prevalent. Therefore, favorable conditions such as high chloride content in aerosols from both anthropogenic and natural sources and high levels of NO_x-O_3 could have**

> **lead to significant levels of $ClNO_2$ to build up and transported to TRF before being completely photolyzed. During the campaign, influence of large biomass burning was negligible as reported in Tang et al. (2018, 2019).”**

(25) Line 189-190: What does “nitrate production was limited due to O3 titration” mean?

The sentence has been removed.

(26) Figure 5(b), Wind directions should be added to see if the morning peak of ClNO2 and the peak of SO2 at 15:00 was related to wind direction change.

We did not observe any changes in the wind direction when the morning peak of $ClNO_2$ was happening.

(27) Line 196-197: an explanation is needed for the choice of the days.

The following sentence has been added and the explanation on the profiles are mentioned in the following sentences.

> (Ln 246) **“...The description on these profiles are further explained in the following sentences.”**

(28) Line 201-202: where is the information on boundary layer height coming from?

The “200 - 300 m” boundary layer height in Line 201-202 was referring to a typical nocturnal boundary layer height during the night, which is not specific for our study. In our study, we used vertical profiles of potential temperature to get the boundary layer heights (Figure 6). Since the DC-8 only flew during the daytime (mostly between 8 am to 4 pm local time), we do not have nighttime measurements of vertical potential temperature profiles during KORUS. Line 201-202 has been removed.

(29) Line 231-234: More detailed discussion of the vertical profiles is needed. How do you define residual layer? In line 210-212, the authors suggested that the ClNO2 in the residual layer could be higher than those at ground surface based on a previous tower measurement in the same region (5 ppb of N2O5 at 360m a.s.l.). Need to reconcile these statements. Was the wind direction different at different altitudes? I suggest the author compare individual vertical profile with ground measurements to better reveal their relationship.

In our study, the boundary layer height was determined based on the vertical profile of the airborne potential temperature measurements. This was averaged during the same timeframe and region as the $ClNO_2$ morning time data shown in Figure 6 (i.e., 8:00 - 8:30 local time). In terms of our statement in ln 210-212, we were suggesting that it is possible that enhanced $ClNO_2$ could have been present in the upper surface layer not the residual layer.

(30) Line 234 and Figure 6(b): The maximum ClNO2 on May 25 appears to be ~200 ppt, while that on May 31 is ~750 ppt and that on June 10 is ~1250 ppt. As to those on other days, dozens samples showed more than 500 ppt even close to 1500ppt in the residual layer (between the nocturnal boundary layer and the boundary layer at midday, in the present study between 200/300m and 1000/2000m). In Figure 6(a), similar results could also be found near the TRF site, over 1000 ppt ClNO2 concentrations were recorded at the height of ~500 m (yellowish). I suggest that the authors revisit the figures and the text.

As in comment #28 and #29, we estimated the nocturnal boundary layer based on the vertical profile of the potential temperature measured on-board the DC-8 in the morning. Based on this measurement, at 8:00-8:30 am local time, the boundary layer height is estimated to be 500 - 600 m. Between this height and above, we did not observe significant $ClNO_2$ levels that could reconcile the ground observations except for the days with colored green square (May 31st), purple triangle (May 25th), and green square (May 31st).

(31) Line 243-251: the evidence for contribution of horizontal transport to the morning peak is not convincing. According to the authors, in half of the days, they measured second peak of ClNO2 at 7-8 am, and in these days, the air masses came from various directions mostly from northwest to southwest and various distance (approximately 200 to 400 Km in 24h) (Fig 8). If the horizontal transport (advection) within the boundary layer is the cause of the second peak of ClNO2, that means in all these directions and distance, there is a bulk of air mass with higher ClNO2 that would constantly arrive at the measurement site at 7-8 am, not before nor after. This is physically not possible.

Following has been added for further discussion:

> (Ln 299-305) **"During KORUS, the DC-8 did not fly to the west of the SMA in the early morning. However, there are large point sources, such as petrochemical facilities and industries, and vehicular emissions to the west and south west of the SMA region. Sullivan et al. (2019) reported that this resulted in enhanced levels of O_3 in receptor regions (i.e., Taehwa Research Forest) downwind when westerlies were prevalent. Therefore, favorable conditions such as high chloride content in aerosols from both anthropogenic and natural sources and high levels of NO_x-O_3 could have lead to significant levels of $ClNO_2$ to build up and transported to TRF before being completely photolyzed. During the campaign, influence of large biomass burning was negligible as reported in Tang et al. (2018, 2019)."**

(32) Line 260-262: Wang et al. 2016 showed much larger contribution of ClNO2 to ozone increase compared to 2% at TRF site, the latter is similar to 3% at Wangdu in Tham et al. (2016).

Line 260 is referring to OH not O_3

(33) Line 270-272: the comment on the result of Tham et al. (2016) and Wang et al. (2016) is an incorrect interpretation of their findings. The three factors (downward transport, horizontal transport and local chemical production) may impact different locations differently. Tham et al. presented evidence for downwind transport in the early morning hours at a polluted rural site in the North China plain. Wang et al. (2016) measured the high ClNO2 plumes at a 974 m mountain- top site and suggested presence of high ClNO2 in the upper boundary layer in south China. They did not say that downward transport should apply to all locations. One has to analyze his/her own case.

We agree on the comment. The following has been added as suggested:

> (Ln 327-332) **"Previous studies have attributed high sustained $ClNO_2$ in the morning to transport from the residual layer (Tham et al., 2016; Wang et al., 2016). In this study, box model runs of heterogeneous and gas-phase production of $ClNO_2$ could not reconcile the observed levels. Moreover, airborne observations in the early morning showed negligible $ClNO_2$ levels in the residual layer in most of the days. Therefore, local transport of $ClNO_2$ from highly polluted airmasses from the west is the most plausible explanation. This shows that different meteorological or chemical conditions of the sites can lead to various causes of high $ClNO_2$ levels in the early morning."**

(34) Figure 7. What was this figure used for?

The reference to figure 9 has been corrected to 7 in the text.

References (*only the references in our responses have been added)

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Integration of Airborne and Ground Observations of Nitryl Chloride in the Seoul Metropolitan Area and the Implications on Regional Oxidation Capacity During KORUS-AQ 2016

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Abstract. Nitryl chloride ($ClNO_2$) is a radical reservoir species that releases chlorine radicals upon photolysis. An integrated analysis of the impact of $ClNO_2$ on regional photochemistry in the Seoul Metropolitan Area (SMA) during the Korean-United States-Air Quality (KORUS-AQ) 2016 field campaign is presented. Comprehensive multiplatform observations were conducted aboard the NASA DC-8 and at two ground sites (Olympic Park, OP; Taehwa Research Forest, TRF), representing an urbanized area and a forested region downwind, respectively. ~~The~~ Positive correlations between daytime Cl_2 and $ClNO_2$ were observed at both sites, which were dependant on O_3 levels. The possible mechanisms are explored through box model simulations constrained with observations. The overall diurnal variations of $ClNO_2$ ~~in~~ at both sites appeared similar but the night time ~~variation~~ variations were systematically different. For about half of the observation days at the OP site the level of $ClNO_2$ increased at sunset but rapidly decreased at around midnight. On the other hand, high levels were ~~sustained~~ observed throughout the night at the TRF site. Significant levels of $ClNO_2$ were ~~sustained~~ observed at both sites for 4-5 hours after sunrise. Airborne observations, box model calculations, and back trajectory analysis consistently show that these high levels of $ClNO_2$ in the morning are likely due to the transport of air masses within the boundary layer. Box model results show that chlorine radical initiated chemistry can impact the regional photochemistry by elevating net ozone production ~~rate up to~~ rates by $\sim$ 25 % in the morning.

1 Introduction

Nitryl chloride ($ClNO_2$) is a night time radical reservoir that generates chlorine radicals ($Cl^{\cdot}$) upon sunrise (R1~~, lifetime of $ClNO_2$~~), with a lifetime (τ_{ClNO2}) of $\approx$ 30 ~~min at midday~~ minutes at midday in the northern hemisphere mid-latitude summer, under clear sky conditions ($J_{ClNO2} \approx 5.47\times10^{-04}$ s^{-1},(Madronich and Flocke, 1998)). It is produced through heterogeneous reaction of chloride (Cl^-) containing aerosols and dinitrogen pentoxide (N_2O_5(g))~~generated from the reaction between the~~ , which is generated from an equilibrium reaction with gas-phase nitrate radical ($NO_3^{\cdot}$) and nitrogen dioxide (NO_2) (R 2-4, (Finlayson-Pitts et al., 1989)). In acidic aerosols (~~< pH 2)~~$\approx$ pH 1.8), uptake of N_2O_5 (g) can also produce gas-phase chlorine (Cl_2~~(g)~~, R5), resulting from ~~an~~ enhanced $ClNO_2$ uptake coefficient of up to 3 - 4 orders of magnitude ~~(Roberts et al., 2008).~~ higher than neutral pH (Roberts et al., 2008). However, this reaction has yet to be proven in ambient conditions.

During the day, N_2O_5 exists at low levels due to its thermal instability (Malko and Troe, 1982) and the short lifetime of NO_3 ($\tau_{NO3} < 5$ s) from photolysis and reaction with NO (Wayne et al., 1991). ~~Reactive chlorine~~ Particulate Cl^- and chlorine containing gas species can come from both natural sources ~~like~~ such as sea salt and biomass burning (Blanchard, 1985; Woodcock, 1953), and anthropogenic sources ~~like~~ such as steel making, incineration, bleaching processes, and ~~coal power plants (Hov, 1985; Reff et al., 2009; Tanaka et al., 2000; Lee et al., 2018)~~coal-fired power plants (Hov, 1985; Reff et al., 2009; Tanaka et al., 2000; Lee et al., 2018; Fu et al., 2018). The efficiency of $ClNO_2$ production depends on heterogeneous loss of N_2O_5, which is a function of the N_2O_5 ~~uptake coefficient on aerosols~~ aerosol uptake coefficient ($\gamma_{\ N2O5}$)~~and~~ , aerosol surface area, and N_2O_5 mean molecular speed, as well as the yield of $ClNO_2$ (ϕ_{ClNO2})(~~$\Phi_{\ ClNO2}$)~~ ~~(Thornton et al., 2003; Schweitzer et al., 1998; Behnke et al., 1997; Hu and Abbatt, 1997; Bertram and Thornton, 2009).~~ (e.g., Thornton et al. 2003; Schweitzer et al. 1998; Behnke et al. 1997; Hu and Abbatt 1997; Bertram and Thornton 2009). The recommended value of γ_{N2O5} in a typical continental boundary layer ranges from 0.01 to 0.04. Recent studies, however, have reported discrepancies between field derived and laboratory parameterized γ_{N2O5} (e.g., Brown et al. 2009; Chang et al. 2016; Morgan et al. 2015; Phillips et al. 2016; McDuffie et al. 2018b; Tham et al. 2016; Wang et al. 2017a, b, c) and ϕ_{ClNO2} (e.g., McDuffie et al. 2018a; Riedel et al. 2013; Ryder et al. 2015; Tham et al. 2018; Thornton et al. 2010; Wagner et al. 2013; Wang et al. 2017b, c). In a nocturnal boundary layer, ClNO$_2$ can accumulate to significant levels due to its long lifetime (τ_{ClNO2} $>$ 30 h) with slow loss mechanisms through heterogeneous uptake (Behnke et al., 1997; Frenzel et al., 1998; George et al., 1995). At sunrise, ClNO$_2$ rapidly photolyzes to generate chlorine radicals (Cl$^{\cdot}$), which can react with most volatile organic compounds (VOCs). For alkanes, Cl$^{\cdot}$ has up to 1 - 2 orders of magnitude larger rate constants than hydroxyl radicals (e.g., $k_{OH+n-C4H10} = 2.4 \times 10^{-12}$, $k_{Cl+n-C4H10} = 2.2 \times 10^{-10}$ at 298 K) (Atkinson, 1997; Atkinson and Arey, 2003). Therefore, Cl$^{\cdot}$ can potentially influence the radical pool (HO$_x$-RO$_x$) and ~~level of~~ ozone (O$_3$) level, which can also affect the formation of secondary aerosols. This influence can be most prominent in the morning when concentrations of other oxidants are low (i.e., NO$_3^{\cdot}$ and $^{\cdot}$OH) (Finlayson-Pitts, 1993; Hov, 1985; Young et al., 2014).

$$ClNO_{2(g)} + hv \rightarrow Cl^{\cdot}_{(g)} + NO_{2(g)} \tag{R1}$$

$$NO_{2(g)} + O_{3(g)} \rightarrow NO^{\cdot}_{3(g)} + O_{2(g)} \tag{R2}$$

$$NO^{\cdot}_{3(g)} + NO_{2(g)} \rightleftharpoons N_2O_{5(g)} \tag{R3}$$

$$N_2O_{5(g)} \xrightarrow{\gamma(N_2O_5), Cl^-(aq)} (2-\phi) * HNO_{3(g)} + \underline{Cl^-_{(aq)} \rightarrow ClNO}\phi * ClNO_{2(g)} \tag{R4}$$

$$ClNO_{2(g)} + Cl^-_{(aq)} + H^+_{(aq)} \rightarrow Cl_{2(g)} + HNO_{2(aq)} \tag{R5}$$

The first ambient ~~measurement~~ measurements of ClNO$_2$ ~~was~~ were carried out by Osthoff et al. (2008)~~at the coast of~~, from a ship sampling along the southeastern U.S. coast in 2006. In that study, ClNO$_2$ was observed up to ∼1 ~~ppb~~ ppbv at night time, particularly during the time period influenced by urban ~~air~~ pollution and ship plumes of the Houston ship channel. Since then, a growing number of measurements reported significant levels of ClNO$_2$, especially in polluted ~~,~~ coastal regions with sources from natural and anthropogenic chloride and nitrogen oxides. Riedel et al. (2012) measured up to ∼2 ~~ppb~~ ppbv of ClNO$_2$ ~~on board a research vessel (Atlantis) during the CalNex 2010 field campaign, and the maximum level was observed in Santa Monica Bay downwind of Los Angeles~~off the coast of Santa Monica Bay, on board the research vessel Atlantis. Recent studies show that high levels of ClNO$_2$ are also present in mid-continental regions. Thornton et al. (2010) measured up to ∼ 400 ~~ppt~~ pptv in Boulder, Colorado, which is ∼ 1,400 km away from the coastline. Mielke et al. (2011) reported up to ∼ 250 ~~ppt~~ pptv in Calgary, Alberta, Canada, during spring, which is ∼ 800 km from the coastline. Back trajectory analysis results showed that the observations were most likely not influenced by marine airmasses. ~~Overall, observations have shown that ClNO~~More recently (in the past 5 years), increasing number of ClNO$_2$ ~~is ubiquitous in the troposphere. However, measurements are still limited, with discrepancies remaining between model and measurements. Modeling studies have consistently suggested the significance of Cl$^{\cdot}$ initiated reactions in regional and global O$_3$ production and in the lifetime of trace gases~~ observations have been conducted in Asia consistently showing significant levels of $ClNO_2$ present in the boundary layer (e.g., ~~VOCs, mercury, etc.)in the troposphere (Knipping and Dabdub, 2003; Tanaka et al., 2000, 2003; Sarwar et al., 2014; Sherwen et al., 2016; Simon et al., 2009)explored the production of~~ Tham et al. 2018, 2016; Wang et al. 2016, 2017c, 2014; Yun et al. 2018; Liu et al. 2017). $ClNO_2$ ~~from sea salt and biomass burning and its impact in the Northern Hemisphere by including $ClNO_2$ formation chemistry in the Community Multiscale Air Quality (CMAQ v 5.0.2) model. The results showed that, compared to the simulations without $ClNO_2$ formation, monthly 8 h wintertime maximum O_3 and ·OH increased up to 7 ppb and 20 % respectively . The production and its subsequent influence was the largest in China and Western Europe. In the Hong Kong-Pearl River Delta (HK-PRD) region, Li et al. (2016) simulated up to ∼ 1 ppb~~ observations at semi-rural (Wangdu of Hebei province) and urban (Hong Kong, Jinan) regions in China have measured up to 2 ppbv and 776 pptv respectively (Tham et al., 2016; Wang et al., 2017b). At the mountain top (957 m above sea level) in Hong Kong, up to 4.7 ppbv of $ClNO_2$ ~~originating from sea salt, biomass burning, and anthropogenic emissions~~ was reported (Wang et al., 2016). The high levels of $ClNO_2$ in these studies were mostly correlated with continental pollution in vicinity (e.g., ~~coal combustion)with the Weather Research and Forecasting coupled with Chemistry (WRF-CHEM)model. This resulted in ∼16 % O_3 increase in the planetary boundary . The assessments using~~ power plant plumes, biomass burning). A recent study by Yun et al. (2018) reported the highest $ClNO_2$ (8.3 ppb), during a severe have event in a semi-rural site downwind of the Pearl River Delta in the winter. Overall, observations have shown that $ClNO_2$ is ubiquitous in the tropospheric boundary layer.

However, measurements are still limited, as discrepancies remain between global chemical transport models ~~are likely lower end estimates since they tend to underestimate~~ and observations. Uncertainties in model simulated $ClNO_2$ ~~due to~~ can arise from limited emission inventories~~. Moreover~~, low resolution of the grid~~can also lead to an underestimation of $ClNO_2$ due to~~ , uncertainties in γ_{N2O5} and ϕ_{ClNO2} parameterization, complexity of the terrain, and meteorological conditions and these have been dealt in previous studies (e.g., Zhang et al. 2017; McDuffie et al. 2018b, a; Lowe et al. 2015; Sarwar et al. 2012, 2014; Sherwen et al. 2017). For instance, smoothing out local $ClNO_2$ peaks ~~and also~~ by diluting local NO_x emissions, ~~that~~ will result in limited NO_3 and N_2O_5 production. According to Sarwar et al. (2012, 2014), the CMAQ model with a finer grid (i.e. 12 km) simulated $ClNO_2$ that corresponded better to the observations, compared to the ~~models~~ model runs with coarser grid size (i.e., 108 km), embedded with similar chemistry. Another modeling study by Sherwen et al. (2017) compared the $ClNO_2$ levels between the GEOS-Chem simulations and observations in inland areas (i.e., London, UK and a mountain top near Frankfurt, Germany) during the summer of 2015. Compared to observations, the simulations underestimated the $ClNO_2$ maxima levels by ∼ 7 times in inland areas.~~Although only a small number of observations in Asia have been conducted in comparison to North America/Europe, previous studies in Asia have consistently shown significant levels~~ (Sherwen et al., 2017). Modeling studies have consistently suggested the significance of $Cl^{\cdot}$ initiated reactions in regional and global O_3 production and in the lifetime of VOCs in the troposphere (Knipping and Dabdub, 2003; Tanaka et al., 2000, 2003; Sarwar et al., 2014; Sherwen et al., 2016; Simon et al., 2009). Sarwar et al. (2014) explored the production of $ClNO_2$ ~~present in the troposphere (Liu et al., 2017; Tham et al., 2016; Wang et al., 2016; ?).~~ from sea salt and biomass burning and its impact in the Northern

Hemisphere by including ClNO$_2$ ~~observations at semi-rural (Wangdu of Hebei province) and urban (Hong Kong, Jinan) regions in China have measured up to 2 ppb and 776 ppt respectively. At the mountain top (957 m above sea level) in Hong Kong, up to 4.7 ppb~~ formation chemistry in the Community Multiscale Air Quality (CMAQ v 5.0.2) model. The results showed that, compared to the simulations without ClNO$_2$ formation, monthly 8 h wintertime maximum O$_3$ and ·OH increased up to 15 % and 20 %, respectively. The impact was the largest in China and Western Europe. In the Hong Kong-Pearl River Delta (HK-PRD) region, Li et al. (2016) simulated up to $\sim$ 1 ppbv of ClNO$_2$ ~~was reported. The high levels of ClNO$_2$ in these studies were mostly correlated to continental pollution from sources nearby~~ originating from sea salt, biomass burning, and anthropogenic emissions (e.g., ~~power plant plumes, biomass burning) .~~ coal combustion) with the Weather Research and Forecasting coupled with Chemistry (WRF-CHEM) model. This resulted in $\sim$16 % O$_3$ increase in the planetary boundary. Another modeling study of WRF-CHEM embedded with an updated chlorine chemistry, simulated 3-6 % of surface O$_3$ increase in the North China Plain and Yangtze River Delta during the summer (Zhang et al., 2017).

East Asian countries are of particular interest due to the rapid economic growth in the past decades with high anthropogenic emissions from densely populated megacities (e.g., Shanghai, Guangzhou, Beijing, Tokyo, Seoul). The majority of the world's ~~mega-cities~~ megacities are situated in coastal regions (Neumann et al., 2015) with high NO$_x$ emissions and abundant sources of chloride from both anthropogenic and natural origin. These regional characteristics likely promote ClNO$_2$ production. Moreover, considering that nearly half the population in the world lives near the coast~~(~~, defined as $<$ 100km from coastline ~~,~~ ~~(Hinrichsen, 1998))~~(Hinrichsen, 1998), a careful evaluation of the impact of ClNO$_2$ on local tropospheric chemistry is crucial.

East Asian countries are of particular interest due to the rapid economic growth in the past decades with high anthropogenic emissions from densely populated megacities (e.g., Shanghai, Guangzhou, Beijing, Tokyo, Seoul). The majority of the world's ~~mega-cities~~ megacities are situated in coastal regions (Neumann et al., 2015) with high NO$_x$ emissions and abundant sources of chloride from both anthropogenic and natural origin. These regional characteristics likely promote ClNO$_2$ production. Moreover, considering that nearly half the population in the world lives near the coast~~(~~, defined as $<$ 100km from coastline ~~,~~ ~~(Hinrichsen, 1998))~~(Hinrichsen, 1998), a careful evaluation of the impact of ClNO$_2$ on local tropospheric chemistry is crucial.
In this study, we present ClNO$_2$ observation results ~~during~~ from the Korean - United States Air Quality (KORUS-AQ) study conducted in the Seoul Metropolitan Area (SMA), South Korea during late Spring (May 2 to June 12, 2016). The field campaign was an international collaboration between the National Institute of Environmental Research (NIER) of South Korea and the National Aeronautics and Space Administration (NASA) of the United States ~~and the National Institute of Environmental Research (NIER) of South Korea~~ with the aim to better understand the impact of ~~mega-cities~~ a megacity on regional air quality. A comprehensive suite of measurements were ~~conducted~~ deployed at two super sites (Olympic Park site, OP; Taewha Research Forest, TRF) ~~, and included airborne observations, that were conducted~~ and aboard the NASA DC-8 to make airborne observations over the South Korean peninsula and the Yellow Sea. ~~By combining airborne and ground measurements from the urban center (OP) and a forested region downwind (TRF), we investigate possible influences~~ We present observational and box model results to evaluate the impact of ClNO$_2$ ~~on tropospheric~~ towards regional air quality in SMA.

2 Methods

2.1 KORUS-AQ 2016 Field Campaign and Observation Sites

We present observations carried out at Olympic Park, (OP; lat:37° 30’ 32.904" N, lon:127° 7’ 20.136" E)~~and ~~, Taehwa Research Forest (TRF; lat: 37° 19’ 14.484" N, lon:127° 18’ 32.58" E) and on the NASA DC-8~~airborne laboratory~~. The two ground sites were within the SMA region, which is the second largest metropolitan area in the world with a population of ∼ ~~25.6 million people~~24 million (Park et al., 2017). As shown in Figure 1(a), the OP site is located in the southern part of Seoul, surrounded by high rise residence buildings and close to major freeways. The TRF site is in the middle of a forested area, ∼ 26 km southeast of the OP site. Previous studies have shown that the TRF site ~~has complex chemistry, ~~is affected by both aged anthropogenic air masses from the city and fresh biogenic emissions from the forest (Kim et al., 2016, 2015). Both sites were ∼ 50 km to the east of the nearest coastline. Figure 1(b) shows the flight tracks of the ~~research flights during the whole campaignwhen $ClNO_2$ was measured~~NASA DC-8, during the KORUS-AQ campaign. Spiral patterns were conducted near the TRF site to measure a vertical profile of the troposphere. Airborne observations were carried out during the daytime, between 8:00 and 17:00 local time. A summary of the analytical techniques of the measurements presented in this study are shown in Table 1. Meteorology during the observation period can be classified into dynamic (May 4th - 16th), stagnation (May 17th - 22nd), transport (May 25th - 31st), and blocking period as shown in Figure 3. During the stagnant period, high pressure system was persistent in the Korean peninsula resulting in local air masses to be more dominant within the SMA compared to the dynamic and transport (May 25nd - 31st) periods. Rex block patterns were observed during the blocking period (June 1st - 6th), which also resulted in more local influence.

2.2 Chemical Ionization Mass Spectrometry and Calibration

A THS Instruments LLC Chemical Ionization Mass Spectrometer (CIMS), using iodide (I^-) as the reagent ion was used for measuring Cl_2 and $ClNO_2$ at the two ground supersites and on the NASA DC-8. The system was similar to what is described in Slusher et al. (2004) and Liao et al. (2011), and the inlet configuration during the campaign is shown in Figure S1. Ambient air was sampled through a stainless steel donut shaped inlet at TRF and a ~~PTFE ~~Polytetrafluoroethylene (PTFE) tube inlet at OP. The stainless steel donut inlet has been shown to effectively avoid wall loss of reactive halogens during previous campaigns (Liao et al., 2011). However, artifacts of $ClNO_2$ ~~of ~~or Cl_2 from interactions on the inlet has been shown to be negligible in various field conditions (Riedel et al., 2012; Thornton et al., 2010; Liao et al., 2014). Therefore, the use of different types of inlets ~~in the ~~(e.g., the use of the donut), described above, at the two ground sites and on the DC-8 is not expected to be an issue for the quantitative comparisons in this study. The sampled air went through the first 3-way valves to be delivered to an ambient or charcoal scrubber mode for background, alternating every 5 minutes. The second 3-way valve was for heated (150 ^{o}C) and unheated cycles~~, and ~~. $ClNO_2$ and Cl_2 were only quantified during the unheated cycles to avoid any potential artifacts ~~, ~~as described in Liu et al. (2017). Additional flow of 4 ~~slpm ~~standard liters per minute (slpm) was drawn at the end of the inlet to reduce the residence time and 1 slpm was sampled into the CIMS. All the inlet parts, after the blower, including the fittings and tubings, were made of ~~Polytetrafluoroethylene (PTFE)~~PTFE. In the flow tube, the target compounds form clusters with I^- (R 5-6, (Huey, 2007; Huey et al., 1995; McNeill et al., 2006)), which were generated by flowing 1 slpm N_2 through a methyliodide (CH_3I) permtube oven maintained at 50 ^{o}C . Polonium (NRD LLC, Static Master, Model: 2U500, Activity: 20 mCi) was used as the radioactive source for ionization. Clusters of Cl_2 isotopes were detected at the mass to charge ratio *(m/z)* of 197 and 199, and $ClNO_2$ was measured at 208 and 210. The natural abundance of Cl_2 and $ClNO_2$ isotopes are approximately 9:6:1 ($^{35}Cl^{35}Cl$: $^{35}Cl^{37}Cl$: $^{37}Cl^{37}Cl$) and 3:1 ($^{35}ClNO_2$: $^{37}ClNO_2$) respectively.

Mass 201 ($^{37}Cl^{37}Cl$) was not considered in the data processing due to artifacts.

$$ClNO_{2(g)} + I^- \rightarrow IClNO_2^-{}_{(g)} \tag{R6}$$

$$Cl_{2(g)} + I^- \rightarrow ICl_2^-{}_{(g)} \tag{R7}$$

Calibrations of Cl_2 and $ClNO_2$ were carried out during and after the campaign. Cl_2 in a cylinder (Airgas, 10 ppm in N_2) was diluted with zero air to be sampled in either ambient or scrubber (charcoal) mode (Figure S1). The Cl_2 in the cylinder was quantified through the method described by Liao et al. (2012) and was 8.84 ± 0.43 ppm. $ClNO_2$ was synthesized, based on Thaler et al. (2011). Briefly, Cl_2 gas in N_2 was passed through a pyrex reservoir (diameter = 1.3 cm, length = 5.5 cm) containing a bed of NaCl (MACRON) and $NaNO_2$ (Sigma Aldrich) with a molar ratio of 10 to 1. This slurry mixture contains NO_2^- that ~~will react~~ reacts with the flowing Cl_2 ~~and~~ to generate $ClNO_2$. The output flow was further diluted with 4 L min^{-1} of zero air in order to sufficiently provide gas flow. The flow containing synthesized $ClNO_2$ was then analyzed at *m/z* of 208 and 210 with the CIMS. NO_2 and NO-NO_y were simultaneously measured with a Cavity Ring Down Spectroscopy (CRDS, Los Gatos Research, detection limit: 10 ~~ppt~~pptv, precision: 50 ~~ppt~~ pptv at 1σ, model: 907-0009-0002) and chemiluminescence (CL, Thermo Scientific, detection limit: 50 ~~ppt~~pptv, model: 42 i) respectively. $ClNO_2$ is detected as NO_y in the CL through conversion to NO on the heated (325 ^{o}C) molybdenum ~~converter.~~ catalytic converter (Williams et al., 1998). The efficiency of the conversion was assumed to be unity. Therefore, $ClNO_2$ could be determined by comparing the three instruments and subtracting the byproducts (HONO and NO_2) from the total NO_y.

2.3 Modeling

We used Framework for 0-D Atmospheric Modeling (F0AM v3.1) for simulating daytime Cl_2 production (Figure 5), in-situ $ClNO_2$ production in the morning (Figure 8), and testing the impact of measured $ClNO_2$ on the regional tropospheric chemistry (~~e.g., O_3 production~~Figure 10). F0AM is a MATLAB based open-source box model. Detailed descriptions of the model can be found in Wolfe et al. (2016). ~~The~~ Each step of the model was constrained with ~~meteorology parameters~~ the averaged meteorology parameters (e.g., pressure, temperature, relative humidity) and trace gases observed in the two ground sites during the campaign. The constrained trace gases include ~~CO,~~ $ClNO_2$, Cl_2, O_3, NO, NO~~,~~$_2$, CO, CH_4, and 20 non-methane hydrocarbons including 8 alkanes (i.e., ethane, propane, iso-butane, n-butane, iso-pentane, n-pentane, n-hexane, and n-heptane), that have relatively high reaction rate constants with Cl~~. For photolysis rate constants ,~~. Photolysis rate constants were derived through the hybrid method (Wolfe et al., 2016) ~~was used and scaled to the rates calculated from the actinic flux measured on-board the DC-8 (< 1km) .~~ in the F0AM box model. This method uses clear sky solar spectra from the tropospheric ultraviolet and visible radiation model (TUV v 5.2) and cross sections and quantum yields suggested by IUPAC. To capture the effects of pollution on photolysis rates, the ratio of the measured J_{NO2} to the F0AM modeled J_{NO2} was calculated. This ratio was then applied to other photolysis rate constants calculated in the model. Measured J_{NO2} was taken from the DC-8 actinic flux measurements (Charged-coupled device Actinic Flux Spectroradiometer; CAFS) when flying near SMA at altitudes under 1 km. A diurnal cycle was applied to the DC-8 measurement to determine j-values at other times of day. Photolysis rate constants of $ClNO_2$, Cl_2, and $ClONO_2$ were not present in the F0AM model and therefore taken directly from the DC-8 measurements. The Master Chemical Mechanism v3.3.1 (MCM) was ~~embedded in the model~~ taken from http://mcm.leeds.ac.uk/MCM ~~, with~~ and embedded in the box model. MCM v3.3.1 has a detailed gas photochemistry (i.e., 5832 species and 17224 reactions), including the oxidation of CH_4 and 142 non-methane primary emitted VOCs (Jenkin et al., 2015). Since MCM v3.3.1 only includes Cl~~·~~· reactions with alkane species, ~~we embedded additional Cl· chemistry~~ additional chlorine chemistry was embedded in the model, similar to what Riedel et al. (2014) reported~~,~~. This was done by including multiple Cl~~·~~· precursors (e.g., Cl_2, $ClNO_2$, HCl, $ClONO_2$, HOCl) and Cl~~·~~· reactions with non-alkane VOCs, such as alkene, alcohol, aromatics, alkynes, ketones, organic acids and nitrates. ~~For simulating $ClNO_2$ production, the model was constrained with airborne observations during the campaign. γ_{N2O5} was calculated from the Bertram and Thornton (2009) study with water content derived from the thermodynamic model Extended Aerosol Inorganics Model (E-AIMS, (Clegg et al., 1998; Friese and Ebel, 2010)), and the measured inorganic aerosol compostion, temperature, and relative humidity. Discussion on how E-AIM was modeled is presented~~ All the reactions embedded in the model can be found in the supplementary of Riedel et al. (2014) and Wolfe et al. (2016). More details on the setup of the box model are in the supplement ~~. The average and median γ_{N2O5} value during the whole campaign were both 0.017. Aerosol surface area was calculated from the measured particle size distributions for particle sizes between 10 nm and 5 μm. The FLEXible PARTicle~~ material (S3). The FLEXible PARTi-cle dispersion model (FLEXPART v9.1, https://www.flexpart.eu) was used for the ~~airmass source contribution~~ air mass source contribution (Figure 3) and backward trajectory analysis ~~.~~ (Figure 9). The backward trajectories reported in our study were initialized 9:00 LST at TRF, following it 24 hours back in time. The trajectories were driven by the National Centers for Environmental Prediction (NCEP) Global Forecast System (GFS) with a 0.25 degree resolution. Influence of air mass originating from the ocean at TRF and OP was calculated every 6 hours following an air mass 5 days back in time. Meteorology was driven by WRF with a 5 km horizontal resolution. Since emissions of CO are very low in the ocean, and assumed to be inert in the model, it was used as a tracer for contribution of air originating from the ocean within a given air mass at each ground site.

3 Results and Discussions

3.1 $ClNO_2$ Observations

Figure 2 shows the temporal variation of trace gases measured during the campaign at (a) the OP site (May 17th - June 11th) and (b) the TRF site (May 5th - June 11th). The OP site, which was located near heavy traffic, showed high levels of NO_x ~~and O_3~~ throughout the campaign. ~~In most of the~~ During most nights (except for May 24th - 26th, 30th - 31st, and June 6th - 7th),

O_3 was completely titrated by NO. On the other hand, at the TRF site, which is a forested region downwind of the urban area, O_3 remained at ∼ 30 ~~ppb~~ ppbv throughout the night. During the measurement period, measureable amounts of $ClNO_2$ were observed at both ground sites (Figure 3). The maximum observed $ClNO_2$ was ∼800 ~~ppt~~ pptv (10 min averaged) and ∼2.5 ~~ppb~~ ppbv (5 min averaged) at the OP and TRF sites, respectively. ~~In~~ At both sites, $ClNO_2$ started accumulating at sunset and rapidly photolyzed upon sunrise, which was ∼5:30 local standard time (LST) during the campaign. Nighttime relationship between $ClNO_2$ and Cl_2 varied day by day and did not show a clear correlation. This implies that the sources of Cl_2 and $ClNO_2$ was not consistent at night. This is similar to Riedel et al. (2012), where they reported a wide range of correlation between Cl_2 and $ClNO_2$ off the coast of LA.

Daytime (11:00 - 18:00, LST) $ClNO_2$ was up to ∼100 ~~ppt~~ pptv at OP and ∼250 ~~ppt~~ pptv at TRF (Figure 4). The level showed a positive correlation ~~to~~ with Cl_2, especially in relatively high O_3 conditions (> 50 ~~ppb~~ppbv). When O_3 was relatively low (< 50 ppbv), Cl_2 production was suppressed, while $ClNO_2$ was not necessarily limited. Excluding the days with low O_3 (i.e., May 26th and 29th for OP and May 6th, 29th, and June 4th for TRF), the relationship between daytime $ClNO_2$ and Cl_2 showed ~~moderate to high correlations~~ positive correlation with R^2 of 0.49 and 0.80 for OP and TRF, respectively. This positive correlation is ~~very similar to~~ consistent with the results reported by Liu et al. (2017) ~~from~~ in the North China Plain~~in June 2014.~~. In their study, up to ∼ 450 ~~ppt~~ pptv of both Cl_2 and $ClNO_2$ was measured during the daytime (10:00 - 20:00, LST), with strong correlation of R^2 = 0.83. Cl_2 levels were also suppressed in low O_3 and OH conditions during low solar radiation periods. Therefore, the authors suggested that daytime Cl_2 levels could be ~~affected by photochemical reactions (or products)~~positively related to photochemical activities. Considering the short lifetime of Cl_2 and $ClNO_2$ during the day (i.e., 11:00 - 18:00 LST in our study), the levels we observed are likely affected through local production. According to Liu et al. (2017), the airmass showed moderate correlation to SO_2 with possible influences from power plants. However, in ~~our~~ this study, the $ClNO_2$ measured at both the OP and TRF ~~site~~ sites was weakly correlated with SO_2 (R^2 = 0.02)~~. Previous studies have shown that N_2O_5 uptake efficiency on aerosols could be affected by organic content of particles (McDuffie et al., 2018b; Thornton et al., 2003). However, we weren't able to identify a correlation.Rather, there is a possibility that the positive correlation~~ , which implies that the air masses that we sampled are not fresh emissions from power plants.

The first possibility we explored is the direct generation of Cl_2 ~~and $ClNO_2$ could be coming~~ from reactions in acidic particles. $ClNO_2$ ~~, generated from N_2O_5 partitioning on Cl^- containing aerosols,~~ is very insoluble ($\gamma_{ClNO2} \approx 10^{-6}$ ~~,~~ (Rossi, 2003)) in near-neutral pH~~, and therefore readily partition into gas-phase.~~However, according to Roberts et al. (2008), ~~in acidic media (< pH 2), $ClNO_2$ has higher uptake coefficients (~~γ_{ClNO2} can increase up to 3 orders of magnitude ~~), which can lead~~ in acidic surfaces (∼ pH 1.8) leading to direct production of gas-phase Cl_2. ~~Indeed, aerosol~~ Aerosol acidity was mostly below pH 2 during the campaign, based on thermodynamic calculations, constrained with airborne observations (Figure S3). Therefore, ~~further investigation is required on the roles of aerosols acidity on the generation of gas-phase~~ the efficiency of this reaction in ambient conditions requires further investigation. Another possibility is the autocatalytic production of Cl_2 ~~and ClNO~~from heterogeneous reactions of gas-phase $ClONO_2$ ~~.~~ (i.e., $ClONO_{2(g)} + Cl^-_{(aq)} + H^+_{(aq)} \rightarrow Cl_{2(g)} + HNO_3$, (Gebel and Finlayson-Pitts, 2001; Gebel and Finlayson-Pitts, 2004)) and HOCl (i.e., $HOCl_{(g)} + Cl^-_{(aq)} + H^+_{(aq)} \rightarrow Cl_{2(g)} + H_2O$, (Vogt et al., 1996)) on particles. These reactions are also favored as particle acidity increases. In order to further investigate its possibility, daytime Cl_2 was simulated by constraining the box model with measurements of $ClNO_2$ and other trace gases corresponding to each data point in Figure 4. Based on the availability of parameters, we were able to simulate 1680 and 1229 runs for the OP and TRF, respectively. This corresponds to more than 96 % of the daytime data points shown in Figure 4. γ_{ClONO2} and γ_{HOCl} were set to 0.06 (Deiber et al., 2004; Deiber et al., 1994; Deiber et al., 1994), which is an upper-limit of previous laboratory studies, and the yields were assumed to be unity. HCl generation from hydrogen abstraction of VOCs by $Cl^{\cdot}$ were included in the mechanisms used in the model runs. The end points of the 72 hour simulation results are presented in Figure 5. As shown in the Figure, the box model simulations were able to reproduce the positive correlation between Cl_2 and $ClNO_2$. Moreover, modeled Cl_2 was suppressed in low O_3 conditions, which corresponds to the observations. This can be explained by $Cl^{\cdot}$ reacting with O_3, producing $ClO^{\cdot}$, leading to gas-phase $ClONO_2$ and HOCl production. These can react on acidic aerosols to generate Cl_2. Sources of $Cl^{\cdot}$ could be from photo-labile gas-phase chlorine compounds (e.g., Cl_2, $ClNO_2$, $ClONO_2$, HOCl) or oxidation of gas-phase HCl by OH. Although the reaction between HCl and OH is relative slow ($k = 7.86 \times 10^{-13}$ cm^3 $molecule^{-1} s^{-1}$ at 298K, (Atkinson et al., 2007)), it has been reported to be a significant source of $Cl^{\cdot}$ in the daytime (Riedel et al., 2012). A sensitivity test was carried out by comparing modeled Cl_2 between runs with and without HCl production from oxidation of VOCs by $Cl^{\cdot}$ (Figure S4 c,d). The results show that production of Cl_2 was suppressed by 40 - 70 % when HCl was not generated in the model. This significant contribution of gas-phase HCl as a $Cl^{\cdot}$ source, should be an upper-limit as the deposition of HCl was not considered in the model. Nonetheless, our analysis leads us to conclude that the mechanisms we have explored could be the main contributors of the daytime Cl_2 production during KORUS-AQ.

3.2 Sources of $ClNO_2$

FLEXPART source contribution analysis shows that the level of $ClNO_2$ at the ground sites ~~highly correlated to~~ was highly correlated with the origin of the air mass (Figure 3). During the nights ~~in red shade~~ shaded in red in Figure 3 (OP: May 20th, 22nd, June 2nd, and 7th; TRF: May 11th, 19th-22nd, June 2nd, and June 6th-7th), there was limited production of $ClNO_2$ ~~. This period corresponded to low contribution of airmasses originating from the ocean and limited particle chloride measured by the~~ at the surface. These periods mostly corresponded to meteorological conditions of stagnation or blocking events, which both resulted in localized air masses to be more dominant with limited influence from the west coast. Stagnation events can be characterized by low wind speeds and increased atmospheric stability, possibly leading to enhanced levels of pollutants like NO_x. Previous studies have shown that these stagnant conditions can result in enhanced levels of N_2O_5 (Baasandorj et al., 2017) driven by high ozone and NO_2. However, $ClNO_2$ production was limited during stagnation events in this study. This is likely due to limited availability of chloride as shown in submicron particle measurements of aerosol mass spectrometer (AMS) at the ground site for OP and airborne over TRF (Figure 3). Whether the chloride is from the ocean or anthropogenic emissions is ~~unclear~~ uncertain since large point sources~~(~~, such as power plants or petrochemical facilities~~)~~, are also present along the west coast of the SMA. ~~At OP, when nitrate production was limited due to O_3 titration, $ClNO_2$ was negligible even with the presence of chloride.~~ On the nights of May 20th and May 22nd, rapid changes in air quality were observed with fast shifts in O_3, SO_2, and CO~~, which also~~. This corresponded with changes in $ClNO_2$ and Cl_2 (Figure ~~S4~~S7). These events suggest the importance of boundary layer advection in controlling the $ClNO_2$ levels in the region.

~~The two ground sites showed rather different diurnal variations , affected by their chemical regimes. Figure 6 shows diurnal averages~~ Different diurnal variations of $ClNO_2$ ~~and other trace gases. Two different diurnal trends of $ClNO_2$~~ were observed between OP and TRF ~~were observed~~(Figure 6). The measurements were averaged over selected days (OP: May 18th-20th, 22nd, 23rd, 29th, June 4th; TRF: May 5th, 8th, 9th, 12th, 17th, 18th, 30th, June 8th, 10th) that showed these two distinct profiles at each site~~, which we will further discuss~~. The description on these profiles are further explained in the following sentences. At the TRF site (Figure 6b), far from direct NO emissions, significant levels of $ClNO_2$ ~~was~~ were sustained throughout the night ~~in~~ during most of the observation period with rapid photolysis upon sunrise. On the other hand, at OP (Figure 6 (a)), $ClNO_2$ started to increase upon sunset, followed by a rapid drop at around 22:00 LST. The trend was consistent with ~~slow~~ slower nitrate radical production rate ~~, calculated from measured NO~~(d[NO_3]/dt = [NO_2~~and~~][O_3~~at the site~~]k, where k = 3.52 × 10^{-17} at 298 K,(Atkinson et al., 2004)) as O_3 was titrated to zero by NO close to midnight. The wind direction, SO_2, and CO did not correlate. ~~The boundary layer at night becomes shallower (200 - 300 m) compared to during the day (1-2 km). The diurnal variations at OP show that NO levels were sustained high in this shallow nocturnal boundary layer throughout the night and often titrated O_3 to zero. Suppressed~~ This suppressed $ClNO_2$ production ~~resulting from NO_3 and O_3 titration by NO has been observed~~ in urbanized regions ~~near surfaces (Osthoff et al., 2018), which is the case of the OP site close to NO emission sources~~with high NO levels, have also been reported by Osthoff et al. (2018). However, significant levels of N_2O_5 and $ClNO_2$ could have been present in the upper part of the surface layer ~~.~~ as shown in previous studies (Baasandorj et al., 2017; Young et al., 2012; Yun et al., 2018). According to Baasandorj et al. (2017), significant levels of N_2O_5 were observed aloft, within the boundary layer, while O_3 was completely titrated near the surface. On the other hand, airborne measurements at the LA basin (Young et al., 2012) showed a relatively uniform $ClNO_2$ profile throughout the boundary layer as O_3 did not change significantly within the measured altitude. During the 2015 Megacity Air Pollution Study (MAPS, Seoul, 2015), a Cavity ~~Enhanced Spectroscopy (CES) instrument~~ Ringdown Spectrometer (CRDS) was installed on top of the Seoul tower in ~~the~~ May - June ~~period for~~ that measured N_2O_5~~measurements~~ , NO_x, and O_3 (Brown et al., 2017). The elevation of the measurement site was 360 m above sea level (ASL), allowing for sampling further away from direct NO emissions. In their study, the average nighttime O_3 mixing ratio was around 50 ~~ppb~~ ppbv and N_2O_5 was observed ~~in most of the nights,~~ most nights, with mixing ratios reaching up to 5 ~~ppb~~ppbv. Therefore, it is ~~reasonable to speculate that $ClNO_2$ could have been present in higher levels than reported in this study. It is~~ very likely that $ClNO_2$ levels higher than the surface measurements could have been present at higher elevation during the observation period.

At both sites, ~~elevated levels of~~ $ClNO_2$ ~~were present 4-5 hours after sunrise. $ClNO_2$, in~~ levels started to increase or sustained after the first 2-3 hours of rapid net loss upon sunrise. In the morning, $ClNO_2$ positively correlated to Cl_2 levels, but ~~$ClNO_2$~~ did not follow the nitrate production rate at the site (Figure ~~S5). A box model run~~S8). Box model simulations, initially constrained with observed $ClNO_2$ ~~at sunrise, simulated rapid photolysis that corresponded to the observation until~~ level, showed rapid photolysis upon sunrise (Figure S5, red dashed line). At TRF, this corresponded to the measurements until 7 ~~am LST (Figure S6). However, between 7 and~~ - 8 am LST, when a second $ClNO_2$ peak was observed ~~at TRF (Figure 6 (b)), a trend that~~ (Figure 6b). This $ClNO_2$ peak in the morning was observed about half the observation days during the campaign. With the net $ClNO_2$ production rate from the observation, and the loss rate from the simulated $ClNO_2$ from photolysis, a production rate of 400

~~ppt~~ pptv h^{-1} would be required to reconcile the observation. In the case of $ClNO_2$ observed on May 5th at TRF (an insert of Figure S6b), a maximum of 2.5 ~~ppb~~ ppbv h^{-1} of $ClNO_2$ production rate was required in the morning to reconcile the observations~~(An insert of Figure S6 (b)). In the case of~~ . At OP, 18 ~~ppt~~ pptv h^{-1} ~~would be~~ was required for the 7 averaged days. The $ClNO_2$ production rate required in the morning at TRF was much higher than the previous studies that have also reported high sustained levels of $ClNO_2$ in the morning (i.e., 20 - 200 ~~ppt~~ pptv h^{-1}) (Faxon et al., 2015; Bannan et al., 2015; Tham et al., 2016). In these previous studies, three possibilities have been suggested that could explain the high sustained levels of $ClNO_2$ in the early morning : 1) entrainment of $ClNO_2$ from residual layer, 2) in-situ generation of $ClNO_2$, and 3) transport of $ClNO_2$ within the boundary layer. Each possibility is explored below.

~~In the~~ At night time, the nocturnal boundary layer is decoupled from the residual layer (Stull, 1988), where the pollution from the previous day resides. Being removed from direct NO emissions near the surface, N_2O_5 can effectively accumulate in the residual layer, with the major loss process being heterogeneous reaction on aerosols. Therefore, high levels of NO_2 and O_3 formed during the day can be trapped in the residual layer ~~and result~~ resulting in significant levels of $ClNO_2$ persisting throughout the night. Figure 7, shows (a) regional and (b) vertical distribution of airborne $ClNO_2$ throughout the campaign in the morning (8:00 - 8:30 LST) over the SMA region (lat: 37^o 12' 0" N - 37^o 38' 60" N, lon: 126^o 54' 0" E - 127^o 47' 60" E). During 3 flights (i.e., May 25th, May 31st, and June 10th), $ClNO_2$ was observed in the residual layer with a max of ∼ 230 ~~ppt. Howeverin rest of the flights,~~ pptv. However, the remaining flights observed an average of ~~only~~ 17 ± 56 ~~ppt~~ pptv of $ClNO_2$ (black circles)~~was observed~~. Even the three days (i.e., May 25th, 31st, and June 10th), that $ClNO_2$ was observed in the residual layer, the level (max 230 ~~ppt~~pptv) could not reconcile the observed levels at the TRF site, which was 342 ± 330 ~~ppt~~ pptv when averaged over the corresponding 3 days at 8:00 - 8:30 LST.

In order to further explore the possibility of in-situ formation, box model simulations of $ClNO_2$ production from heterogeneous reaction of N_2O_5 and chloride containing aerosols were conducted. N_2O_5 was calculated assuming a photo-stationary state of NO~~$_3$ (Brown et al., 2005)and aerosol~~ $_3$ (Brown et al., 2005). Aerosol surface area was taken from airborne observations over TRF. Based on the box model results in Figure ~~10~~8, even with an assumption of 100 % yield, $ClNO_2$ from heterogeneous reaction was not able to reconcile the observed level. ~~The box model analysis was carried out to also explore the possibility of~~ Box model simulation on gas phase production of $ClNO_2$ (i.e., $Cl\cdot_{(g)} + NO_{2(g)} + M \rightarrow ClONO_{(g)} + M$, $Cl\cdot_{(g)} + NO_{2(g)} + M \rightarrow ClNO_{2(g)} + M$) showed at most 2-10 pptv of $ClNO_2$ ~~(Figure S8). The simulations show that only 2-10 ppt of $ClNO_2$ and ClONO can be produced during the day.~~ and ClONO (Figure S6).

Therefore, the third possibility, local transport within the boundary layer, would be the most likely explanation for the high $ClNO_2$ in the morning based on our analysis. Although $ClNO_2$ readily photolyzes during the day ($\tau_{ClNO2} \approx$ 30 min at midday), the lifetime could be significantly long enough in the early morning to allow for transport of $ClNO_2$ to the ground sites. Based on the NCAR ~~Tropospheric Ultraviolet and Visible (~~TUV v5.2 ~~)~~ model, the lifetime of $ClNO_2$, averaged between 5:30 and 8:30 LST was ∼ 2 hours ~~during the campaign,~~ under clear sky conditions. Figure 9 shows back trajectory analysis initiated at 9 am local time at TRF. At high $ClNO_2$ days with the morning peaks, most of the air masses ~~originiated~~ were from the west. ~~In the west, there could have been favorable conditions for $ClNO_2$ to build up,~~ During KORUS, the DC-8 did not fly to the west of the SMA in the early morning. However, there are large point sources, such as petrochemical facilities and industries, and vehicular emissions to the west and south west of the SMA region. Sullivan et al. (2019) reported that this resulted in enhanced levels of O_3 in receptor regions (i.e., Taehwa Research Forest) downwind when westerlies were prevalent. Therefore, favorable conditions such as high chloride content in aerosols from both anthropogenic and natural sources and high levels of NO_x-O_3 ~~to generate N_2O_5 at night. Therefore,~~ could have lead to significant levels of $ClNO_2$ ~~produced during the night in the west could have been~~ to build up and transported to TRF before being completely photolyzed. During the campaign, influence of large biomass burning was negligible as reported in Tang et al. (2018, 2019).

3.3 Impacts of $ClNO_2$ on O_3

Cl· produced from $ClNO_2$ photolysis can influence the local air quality through reactions with VOCs followed by enhanced production of O_3. ~~In order to investigate the~~ The possible impact of Cl· initiated reactions on the local chemistry ~~, we carried out a box model analysis constrained with observations of~~ were investigated by running box model simulations constrained with measured $ClNO_2$~~, NO and VOCs described in the method. The~~ . A 24 hour diurnal variation of $ClNO_2$ ~~constrained in the box model was averaged for the same days shown~~ was averaged over the same selected days as in Figure 6, and these were constrained throughout the model simulations. The results ~~show~~ illustrate that when the model was constrained with $ClNO_2$ and Cl· initiated chemistry, higher levels of O_3 were simulated (Figure 10) compared to the base runs without $ClNO_2$. The averaged net O_3 production rate was enhanced by up to 2 % and 25 % at OP and TRF in the morning and by 1 % and 2 % when averaged during the day. ~~Although the OP site has higher alkane levels~~ The OP had 7 times lower Cl· than the TRF site ~~, Cl in the morning were around 7 times lower due to the~~ due to low $ClNO_2$ levels (∼60 ~~ppt~~pptv) in the morning. For ·OH, the net production rate at TRF increased by 2 % in the morning. The results particularly from TRF are comparable with the previous study in the mountaintop site in Hong Kong, China (Wang et al., 2016). The enhancement of ~~ozone~~ O_3 (max - min) was higher than their moderate $ClNO_2$ case (11 %) but lower than the high $ClNO_2$ plume case (41 %).

4 Conclusions

~~A comprehensive suite of~~ Comprehensive measurements of $ClNO_2$, Cl_2, other trace gases, and aerosol concentrations and properties have been conducted on the NASA DC-8 and at two ground sites during the KORUS-AQ 2016 field campaign. The observed averaged diurnal variations are largely consistent with the previous observations and our understanding on the photochemistry of $ClNO_2$. ~~In addition, the~~ The presence of $ClNO_2$ was substantially suppressed during strong stagnation events, which could have prevented the transport of chloride ~~from~~ near the coast. ~~High levels of~~ During the night, Cl_2 and $ClNO_2$ ~~were sustained for~~ levels were not correlated while moderate to strong positive relationships were observed at daytime. Through box model simulations, we presented a quantitative analysis on the daytime observations. The results showed that heterogeneous reactions of $ClONO_2$ and HOCl in acidic aerosols may be responsible for the positive correlation between Cl_2 and $ClNO_2$, as well as its dependency on O_3. The second $ClNO_2$ peak in the morning, observed 4-5 hours after sunrise, ~~which requires significant production~~ required a significant source of $ClNO_2$ (up to 2.5 ~~ppb~~ ppbv h^{-1}). ~~We did not find any empirical evidence to support the hypothesis raised by previous studies , where they~~ Previous studies have attributed high sustained ClNO$_2$ in the morning to transport from the residual layer ~~Tham et al. (2016); Wang et al. (2016). Moreover~~(Tham et al., 2016; Wang et al., 2016). In this study, box model ~~simulations~~ runs of heterogeneous and gas-phase ~~reactions only generated about 10 ppt~~ production of ClNO$_2$ ~~, and thus~~ could not reconcile the ~~discrepancies. Rather,~~ observed levels. Moreover, airborne observations in the early morning showed negligible ClNO$_2$ levels in the residual layer in most of the days. Therefore, local transport of ClNO$_2$ from highly polluted airmasses ~~, originating~~ from the west ~~,~~ is the most ~~likely explanation.~~ plausible explanation. This shows that different meteorological or chemical conditions of the sites can lead to various causes of high ClNO$_2$ levels in the early morning. Finally, box model simulations constrained with observations suggest that Cl· initiated chemistry can lead up to ∼25 % increase of net O$_3$ production rate in the morning.

Data availability. Dataset used in this study is open to public and can be downloaded at https://www-air.larc.nasa.gov/missions/korus-aq/

Author contributions. DJ, RS, DG, YL, DT, SK, and GH designed and executed field measurements for collecting ClNO$_2$ and Cl$_2$; BAN, JLJ, and PCJ provided the airborne AMS data; CK ran the FLEXPART analysis; TM and JS provided O$_3$ measurements; DRB provided the WAS data; DS and AG provided the PTR-ToF-MS data; RL provided NO$_x$ and O$_3$ data; BA provided the data from LARGE; SRH and KU provided data from CAFS; HS provided AMS data at OP; SH provided HCHO measurements at TRF; YL, DK, and JA provided CO measurements at TRF. DJ and SK prepared the original manuscript, and all other authors contributed in editing the manuscript.

Acknowledgements. This study is supported by NASA (NNX15AT90G) and NIER. CU HR-AMS measurements and pH and aerosol liquid water calculations (BAN, PCJ, and JLJ) were supported by NASA grant NNX15AT96G and 80NSSC18K0630. We thank the Wisthaler research group (University of Oslo, University of Innsbruck) for providing airborne VOC data, John Crounse and Paul Wennberg(CALTECH) for the HNO$_3$ data, Hwajin Kim (Korea Institute of Science and Technology) for the discussions on aerosol composition, and Siyuan Wang (NCAR) for discussions on box model simulations. The authors appreciate logistical support from the research and supporting staff at Taehwa research forest operated by Seoul National University.

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Table 1. Summary of the measurements carried out during the KORUS-AQ 2016 field campaign, used in this study.

Compound	Method		
	TRF	OP	DC-8
NO	^{a}CL	^{b}FRM	^{c}CL
NO_2	^{d}CRDS	^{e}CAPS	^{c}CL
O_3	^{f}DIAL	^{g}SL-UV	^{c}CL
SO_2	^{h}PF	^{i}UV florescence	x
CO	^{j}IR	^{k}NDIR	x
$ClNO_2$,Cl_2	^{l}CIMS	^{l}CIMS	^{l}CIMS
VOCs	^{m}PTR-ToF-MS	^{o}QCL	^{p}PTR-ToF-MS
	^{n}TILDAS		^{q}WAS
chloride (< 1 μm)	x		
nitrate (< 1 μm)	x	^{r}ToF-AMS	^{s}HR-ToF-AMS
sulfate (< 1 μm)	x		
surface area (< 200 *nm*)	x	x	^{t}SMPS
surface area (200 *nm* - 5 μm)	x	x	^{u}LAS
Jvalues	x	x	^{v}CAFS

^{a}Chemiluminescence with a molybdenum converter (Thermo Scientific 42i - TL), ^{b}Chemiluminescence detector (Federal Reference Method, Teledyne T200U), ^{c}NCAR 4-channel chemiluminesecence (Weinheimer et al., 1994), ^{d}Cavity Ring Down Spectroscopy (Los Gatos Research NO_2 analyzer), ^{e}Cavity Attenuated Phase Shift spectroscopy (Teledyne T500U CAPS analyzer), ^{f}NASA TROPospheric OZone DIfferential Absorption Lidar (Sullivan et al., 2014), ^{g}UV photometric method (2B 211), ^{h}Pulsed fluorescence method (Thermo Scientific 43i-HL), ^{i}UV florescence method (KENTEK), ^{j}Infrared CO analyzer (Thermo Scientific 48i-HL), ^{k}Non-Dispersive Infrared CO analyzer (KENTEK), ^{l}Chemical Ionization Mass Spectrometer (Slusher et al., 2004), ^{m}Proton-Transfer-Reaction Time-of-Flight Mass Spectrometer (IONICON), ^{n}Tunable Infrared Laser Direct Absorption Spectroscopy (Aerodyne), ^{o}Quantum Cascade Laser spectrometer (Aerodyne), ^{p}University of Oslo/Innsbruck Proton-Transfer-Reaction Time-Of-Flight Mass Spectrometer (Müller et al., 2014), ^{q}Whole Air Sampler (Colman et al., 2001), ^{r}Aerosol Mass Spectrometer (Aerodyne), ^{s}University of Colorado, Boulder,Aerosol Mass Spectrometer (Nault et al., 2018), ^{t}NASA, Scanning Mobility Particle Sizer, ^{u}NASA, Laser Aerosol Spectrometer, ^{v}NCAR, Charged-coupled device Actinic Flux Spectroradiometer (Shetter and Müller, 1999)

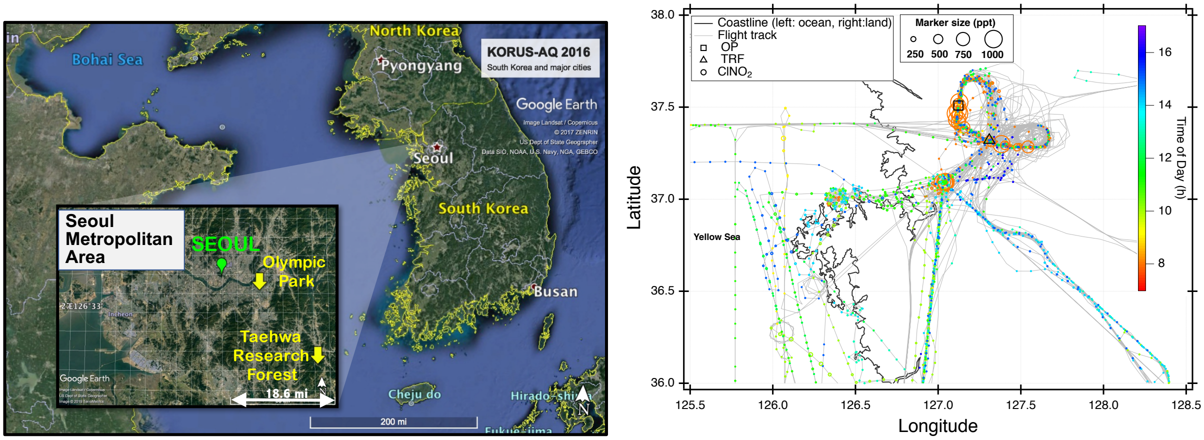

Figure 1. (a) Location of two ground sites (Taehwa Research Forest and Olympic Park) where the chemical ionization mass spectrometer (CIMS) was installed during the KORUS-AQ 2016 field campaign (b) Airborne measurements of $ClNO_2$ and DC-8 flight tracks during the whole campaign. The $ClNO_2$ data points are 60 sec averaged and color coded by time of day of the measurement. The marker size is proportional to the mixing ratio of $ClNO_2$.

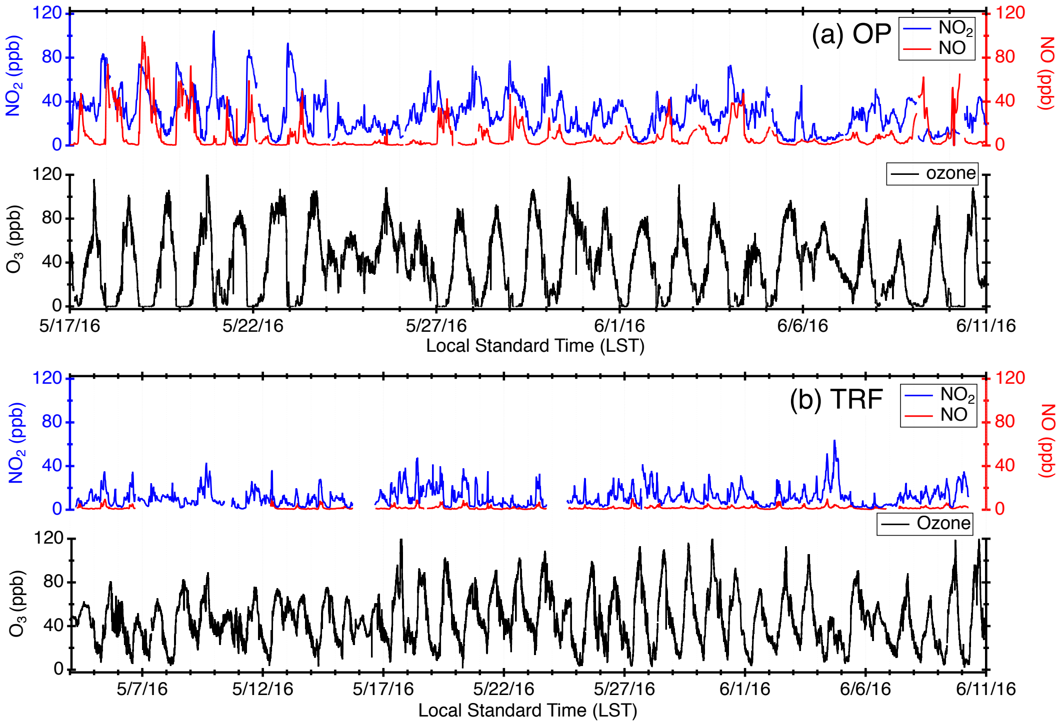

Figure 2. Temporal variation of trace gases measured at the (a) Olympic Park site (OP) and (b) Taehwa Research Forest (TRF). For both OP and TRF, the frequency of the averaged data is 10 min for NO_x and 1 min for O_3.

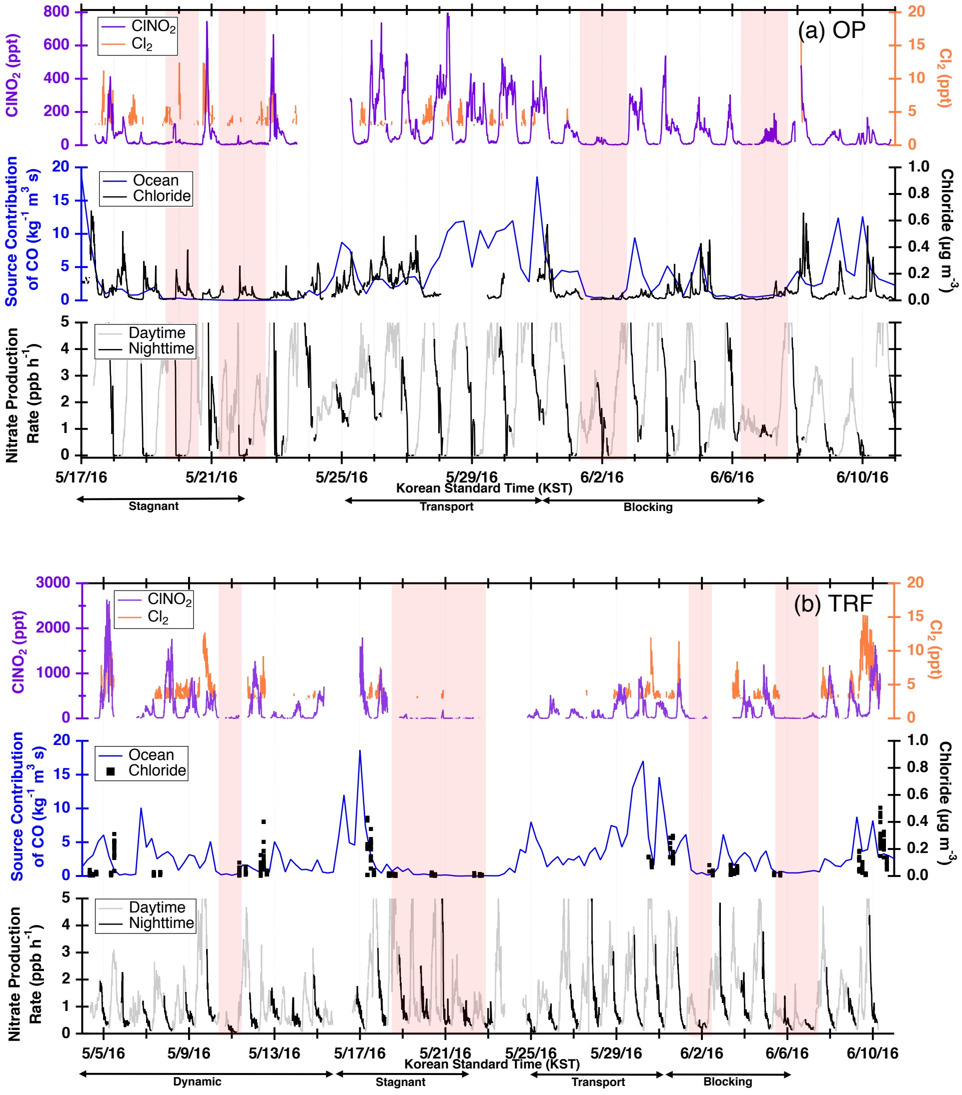

Figure 3. ClNO$_2$ and Cl$_2$ observation results at (a) OP and (b) TRF averaged over 10 min and 5 min respectively. FLEXPART back trajectory analysis were made for source contribution of CO-like substance originating from the ocean, assuming inert CO. Aerosol chloride mass concentration (ambient μg m^{-3}) was measured at the ground for the OP site and on the NASA DC-8 for TRF. For the airborne chloride, measurements below 1 km over the TRF site is shown. Red shades are the time frames with limited ClNO$_2$ production.

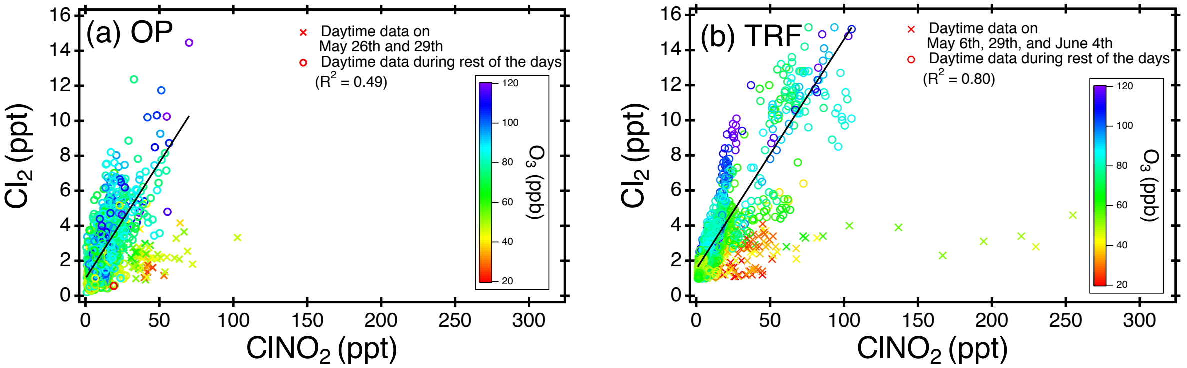

Figure 4. Scatter plot of daytime (11:00 - 18:00 local time) ClNO$_2$ and Cl$_2$ at (a) OP and (b)TRF, color coded with measured O$_3$. 5 min averaged data for the whole campaign were used for both sites.

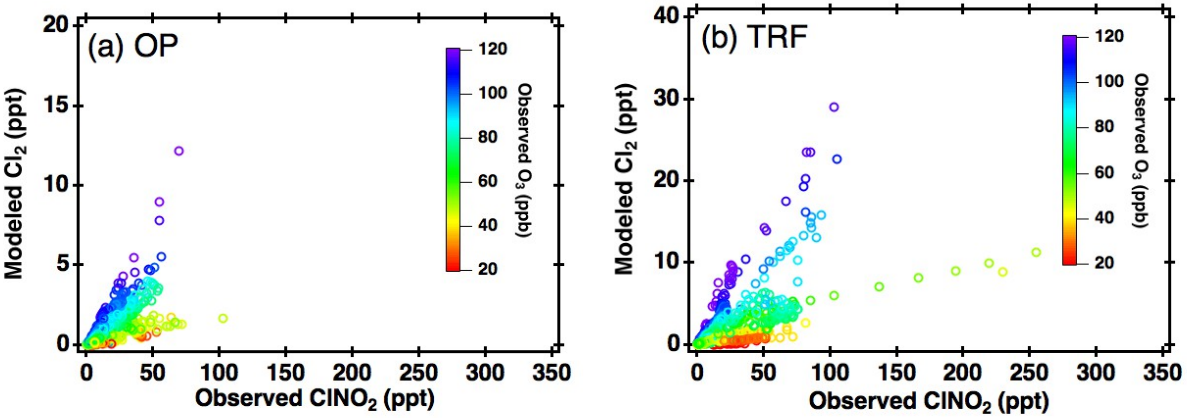

Figure 5. Correlation between box model simulated daytime (11:00 - 18:00 local time) Cl_2 and measured $ClNO_2$ at (a) OP and (b)TRF, color coded with measured O_3.

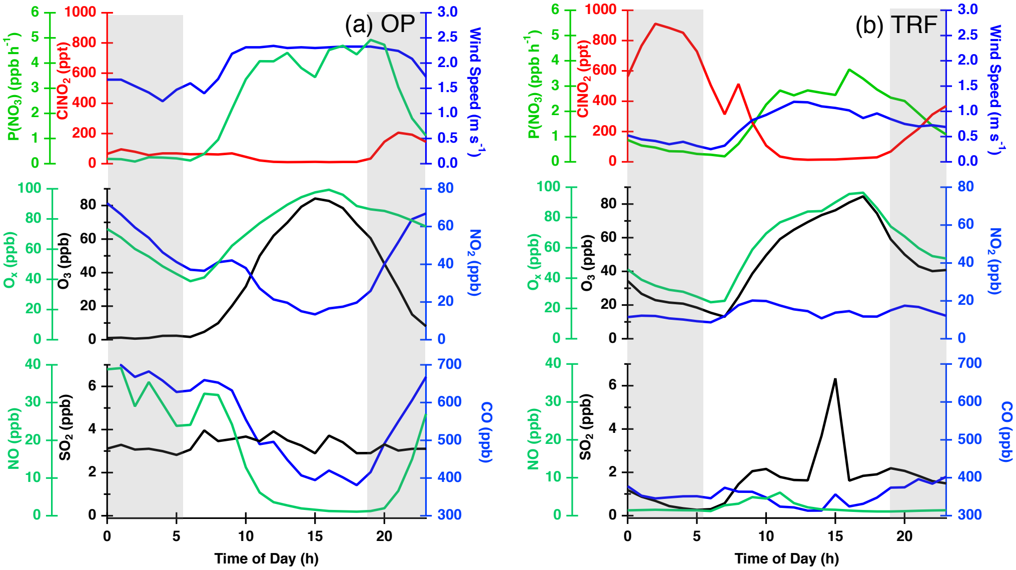

Figure 6. Diurnal variation of ClNO$_2$ and other trace gases measured during the campaign and averaged over selected days at (a) OP (7 days) and (b) TRF (9 days). Night time is shown as grey shades.

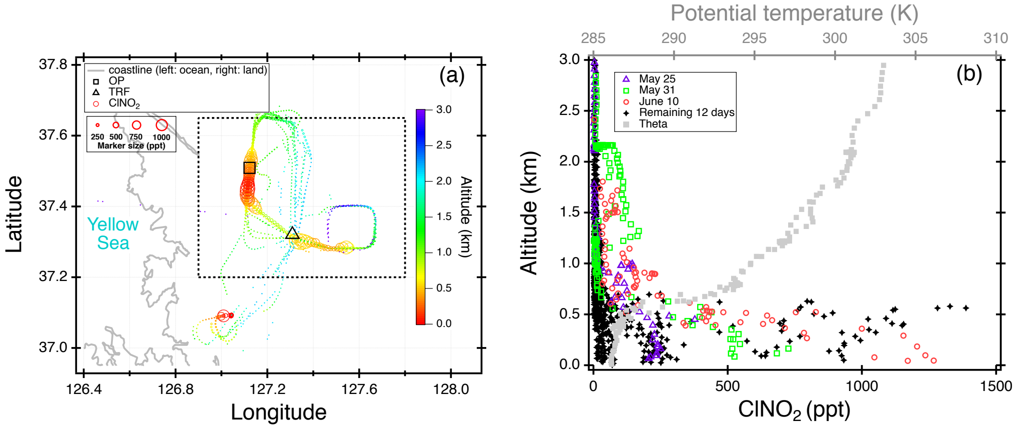

Figure 7. (a) Regional and (b) vertical distribution of airborne $ClNO_2$ measured over the Seoul Metropolitan Region (SMA) in the morning (8:00 - 8:30 local time).

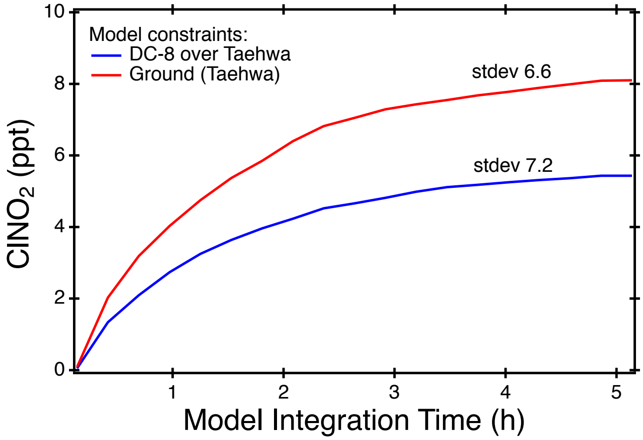

Figure 8. Steady state $ClNO_2$, simulated from a box model constrained with airborne measurements (blue) and ground site data from TRF (red), when there was a morning $ClNO_2$ peak. Averaged values of the model runs are shown here with standard deviations.

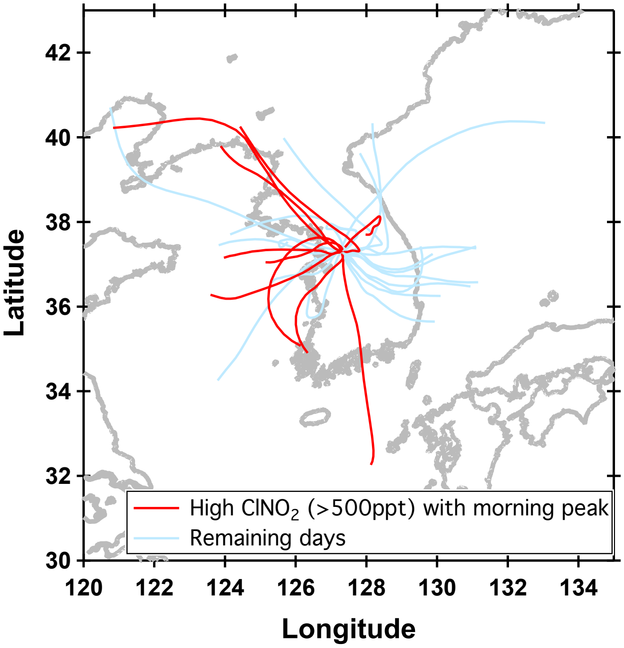

Figure 9. FLEXPART back trajectories from Taehwa Research Forest. Trajectories were initialized at 9 am local time and went 24 h backwards. Only the center trajectories with the highest percentage of airmasses are presented. Trajectories for days with high levels of $ClNO_2$ (> 500 pptv) at night are in red and the remaining days are shown in sky blue.

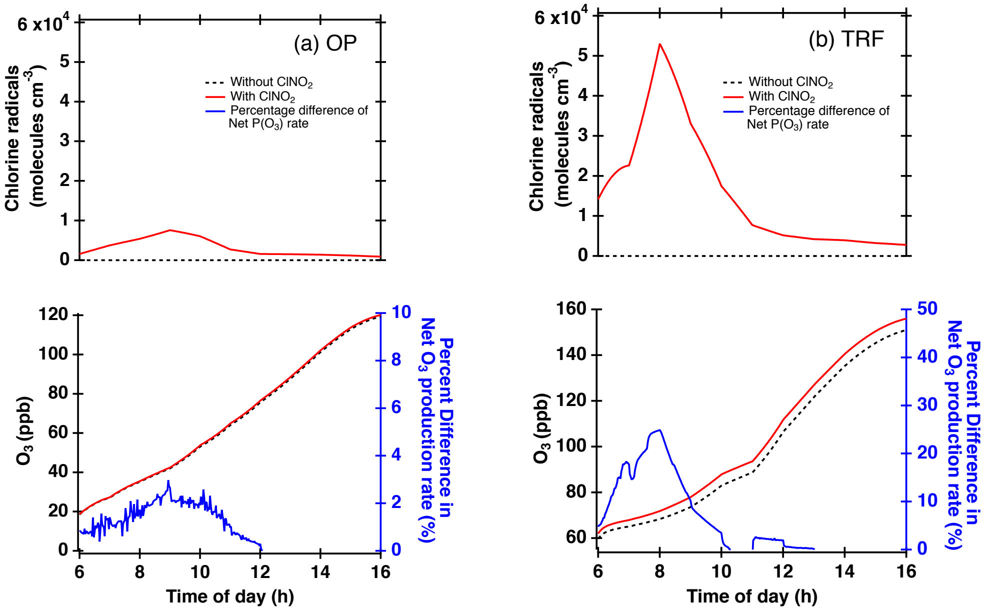

Figure 10. Box model simulations of chlorine radicals and O_3 at (a) OP and (b) TRF, constrained with $ClNO_2$ and other trace gases observed during the field campaign. Percent difference of net O_3 production rate (NetP(O_3), blue line) was calculated from the difference of the NetP(O_3) between simulations with and without $ClNO_2$ constrained in the model (i.e., 100*(w$ClNO_2$ - wo$ClNO_2$)/wo$ClNO_2$).