R1 - Review of "Integration of Airborne and Ground Observations of Nitryl Chloride in the Seoul Metropolitan Area and the Implications on Regional Oxidation Capacity During KORUS-AQ"

The authors have provided a thoughtful response to the original review. While the manuscript has been greatly improved, there are a few remaining issues that have not been fully addressed in the updates. The primary concerns are (1) the description of each type of box model simulation and (2) the role of vertical vs. horizontal mixing as a primary source of surface-level $ClNO_2$. In the comments below, the original review comments are in gray, the author response is in blue, and the new comments are in red. A few minor comments are at the end in black.

Comments on Author Response

Comment (1) - 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 $N_2 O_5$ (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)."**

Lines 112 – 114 – The authors have improved the manuscript with a description of the meteorological events observed during the study. However, neither Figure 2 nor 3 appear to explicitly show the meteorological conditions as described in this section. The only indicator seems to be the source contribution from the ocean. Please clarify how the different meteorological conditions are represented in these time series. In addition, please define or explain a 'Rex block pattern'.

Line 232 – Same comment here. It is not clear how Figure 3 represents the different meteorological conditions experienced at the sites. Please update the figure or add clarification in the text.

Line 238 – Please specify that the stagnation events reported in Baasandorj et al., 2017 are during the winter season.

Comment (2) - 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."**

Section 2.3 – While the authors have provided many details in their update, it remains unclear exactly how the simulations were setup, how many different types of simulations were run (and what the similarities and differences were), as well as important missing details about the model treatment of boundary layer dynamics and deposition.

First, the authors need to state explicitly in the Section 2.3 of the main text what the duration of each model simulation was (i.e., 72 hours?) and the frequency at which the model was constrained with observations (i.e. every 100 minutes?). Currently, the supplement indicates a discrepancy where it states that the model duration is 1 day. However, it becomes apparent later in the main text that (at least) two different types of simulations were conducted (both 72 hour and 1 day simulations). The setup details (e.g., duration, initialization time, constraint frequency, any chemical/physical differences, number of simulations, etc.) are needed for each type of simulation in order to avoid confusion later. For instance, on Line 219, it is unclear what the 'end points' of 72-hour simulations are. Are these final mixing ratios at the end of different simulations? What time of day are the simulations set to end? How many individual simulations were run and what were the differences between them? At the moment, Section 2.3 reads as if there was only one type of simulation used.

Second, the authors need to include additional information about how boundary layer dynamics are treated in both the 72 and 24-hour simulations. For instance, how does the model treat the separation of the surface and residual layer at night and the entrainment of O_3 in the morning? Does the model include deposition? These details are missing from both the main text and the supplement and are important for the accurate simulation of O_3 production.

Third, on line 34 in the supplement, it is unclear what the authors mean by 'all the measured parameters'. Does this mean that all concentrations are held constant? All rate constants? All photolysis frequencies? Please clarify.

Comment (3) - 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."**

Paragraph on line 246 –In this section, instead of referring to the boundary layer at night, please clarify that the boundary layer splits into a nocturnal surface layer and a residual layer. This distinction will help clarify that the authors are discussing N_2O_5 and $ClNO_2$ profiles at night in this section. In addition, since this is the first discussion of elevated N_2O_5/$ClNO_2$ aloft, it seems to make more sense to move lines 278-281 to line 255.

Line 256 – Suggest changing this sentence to, "According to Baasandorj et al. (2017), O_3 was completely titrated at the surface in Salt Lake Valley, Utah, while elevated mixing ratios of N_2O_5 were observed at 155m AGL, at a site along the valley wall." These changes are meant to clarify that Baasandorj study reported ground measurements only, whereas the current text indicates that aircraft or tower measurements were collected.

Line 258 – Specify the altitude range of data reported by Young et al. (2012).

Comment (4) - 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)."**

Lines 277 & 294 – Please clarify, when the authors state, 'transport', do they mean *only* horizontal transport or *both* vertical and horizontal transport? It seems that the authors are arguing that high $ClNO_2$ levels are being transported horizontally to the ground sites from other (non-measured) sources to the west of the sites. It also seems possible, however, that $ClNO_2$ is being produced aloft at night in the west and these concentrations are being transported both horizontally and vertically in the morning as the air parcel moves. Please clarify and discuss any evidence for the role of horizontal vs. vertical transport from the western region.

In light of this possibility, it seems that the role of vertical mixing cannot be completely ruled out, as is currently suggested in the discussion section. I would suggest that the paragraph starting on line 278 clarify that while aircraft measurements collected to the south/east of the sites provided limited evidence of the role of vertical mixing contributions to elevated surface-level $ClNO_2$, there may be enhanced vertical contributions from air parcels arriving from the west.

Comment (5) - 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 3 – With the author updates, it is now clear why the Cl_2 data appear to have an offset in Figure 3. The below LOD data points, however, appear to be included in later figures, such as Figure 4. Please clarify why below LOD data were removed in Figure 3 and not others.

Comment (6) - 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 ± 4 1 $\mu m^{2}\ cm^{-3}$ were estimated for particle sizes between 10 nm and 5 μm."

Supp. Line 38 – Please clarify why dry surface area was used to calculate gamma(N_2O_5). This assumption will artificially increase the N_2O_5 rate constant as gamma(N_2O_5) is typically calculated using the wet aerosol surface area.

Comment (7) - 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) :**
# of reactions
$d[O_3]/dt = O_3 \text{ production rate} - O_3 \text{ loss rate} = \sum f_i \times (\text{product of reactants})_i \times k_i$

Equation 1 – Please check the formatting of this equation in the final manuscript.

Additional Minor Comments:

Line 6 – Change to, '…sites, the slope of which were dependent on O_3 levels."

Line 29 – The authors have appropriately cited the discrepancies between field and laboratory results. It remains unclear, however, where the 'recommended' value comes from. Could the authors please specify. I only ask because both field and lab measurements have reported a wide range of values from $< 1 \times 10^{-4}$ to > 0.04.

Line 62 – Change to, '…reported the highest-recorded mixing ratio of $ClNO_2$ (8.3 ppbv)…'

Paragraph staring on line 65 – The authors might also want to include the recent modeling paper by X. Wang (2019) ACP, who simulated $ClNO_2$ production in GEOS-Chem and found large contributions of this chemistry to daytime radical production.

Line 112 – Figure 3 is referenced before Figure 2.

Line 122 – Change, 'However' to 'In addition'

Line 129 – What is the 'blower' that the authors refer to? This isn't indicated in Figure S1.

Line 149 – There are NO_y species in addition to HONO and NO_2 that would need to be subtracted to quantify the ambient $ClNO_2$. These include, but are not limited to N_2O_5, NO_3, NO, and HNO_3. Please clarify whether these species were included in the subtraction or note that they were not and state the resulting bias.

Line 165 – Just to clarify, $ClNO_2$, Cl_2, and $ClONO_2$ photolysis frequencies were not included in TUV, but the authors incorporated the measured values into the F0AM model, correct? If so, please adjust the text accordingly.

Line 188 – Please report observations averaged over the same time period (i.e. 10 minutes) so that mixing ratios at different sites can be compared directly. Check for consistency throughout the manuscript when mixing ratio from the aircraft and ground sites are reported and compared to each other.

Line 191 – Different nighttime correlations between Cl_2 and $ClNO_2$ may not only indicate different sources, but potentially different loss processes as well.

Line 216 – Change, '1229 runs…' 'to '1229 points…'. Unless the authors did run 1229 simulations that were each 72-hours in duration.

Line 310, 335 and abstract – The authors should specify that the percent increases only account for the chemical production of O_3. This is an important point because net O_3 production observed from the ground will also be influenced by the morning entrainment of O_3 from aloft (which doesn't seem to be included in the model here).

Line 324 – Change 'on the' to 'of the'

Figure 4 – It is unclear why modeled Cl_2 is compared to observed and not modeled $_{\mathrm{ClNO2}}$. This comparison could help provide additional validation of the model.

Supplement:
Section S3. – When the authors state that 'average' values were used, does that mean that a single value was used throughout the entire model simulation? Please clarify. Also, in this section, please change Figure references 'Figure 4' and 'Figure 5' to 'Figure S4' and 'Figure S5'.