Response to interactive comment on “Significant production of $ClNO_2$ and possible source of Cl_2 from N_2O_5 uptake at a suburban site in eastern China” by Men Xia et al. from anonymous Referee #1

The manuscript "Significant production of ClNO2 and possible source of Cl2 from N2O5 uptake at a suburban site in eastern China" by Xia et al. presents a set of measurements of nitryl chloride (ClNO2) and molecular chlorine (Cl2) taken near the city of Nanjing, in Eastern China, in April 2018. The authors use this dataset, and related observations, to analyze the formation of ClNO2 and Cl2 and to draw conclusions about the underlying multiphase chemical mechanism. The paper is well written and the data are presented in a clear and concise way. The analysis and the results are sound and the authors propose some novel ideas that will certainly be of great interest to the community. I only have a few, fairly minor, comments, but overall I think this paper is suitable for publication in Atmospheric Chemistry and Physics.

Response: we appreciate the reviewer for the positive comments and helpful suggestions. Below is the response to each comment. The reviewers’ comments are italicized followed by our responses and changes shown in blue and red, respectively. And the corrections are also marked as red color in the revised manuscript. Please note that the line numbers mentioned below refer to the original submission (line numbers in the revised version have changed).

General Comments ——————-

In Section 3.3, the authors discuss the calculation of the yield of ClNO2, comparing the "BT" parametrization by Bertram and Thornton (2009) with a new parametrization. Looking at figure 4, I am not sure I completely agree with the author’s interpretation. The new parametrization proposed in this paper does indeed agree better with the observations for yields between 0.4 and 0.6; however I would argue that the agreement is worse than the BT parametrization at higher yields (around 0.8) and only slightly better at lower yields (below 0.4). Clearly, the relationship between the various parameters is more complicated than either parametrization assume, and perhaps this suggests that there are other parameters that are not currently taken into account which play a role. In any case, I suggest that the authors revise their statements in this section (and the related parts of the conclusions and the abstract) to be more accurate.

Response: we appreciate and agree your comment on our interpretation of the performance of the new parameterization at higher yields (0.75~1). We also agree that other unconstrained factors may influence $\varphi(ClNO_2)$. We have revised the relevant texts as below.

Revision in the main text:

Line 329-330 (section 3.3): The parameterized $\varphi(ClNO_2)_{BT+Org}$ better matches the observed $\varphi(ClNO_2)$ at low to median yields (0~0.75) and the R^2 and slope values in the linear regression are closer to 1 (Fig. 4b). However, the parameterized $\varphi(ClNO_2)_{BT+Org}$ is smaller than the observed $\varphi(ClNO_2)$ at high yields (0.75~0.9), which may be attributable to other unconstrained factors in the parameterization, e.g., mixing state and phase state issues.

In Section 3.4, the authors propose a mechanism for the production of Cl2 during the night.

The key point of the argument is that, for the observations to be consistent with each other, g(ClNO2) must decrease and there is not really a good explanation for why that would be the case. Although I agree with this logic, there may be other parameters that influence g(ClNO2) besides Cl-, H+ and Dp. In particular organics, which are mentioned as important for g(N2O5) in the previous section may inhibit the uptake of ClNO2 as well. Likewise, RH, other aerosol components, and perhaps even temperature, may have an effect. I appreciate that it is not possible to exhaust all possible parameters but I think the authors should expand their analysis a little bit here, to make a more robust case.

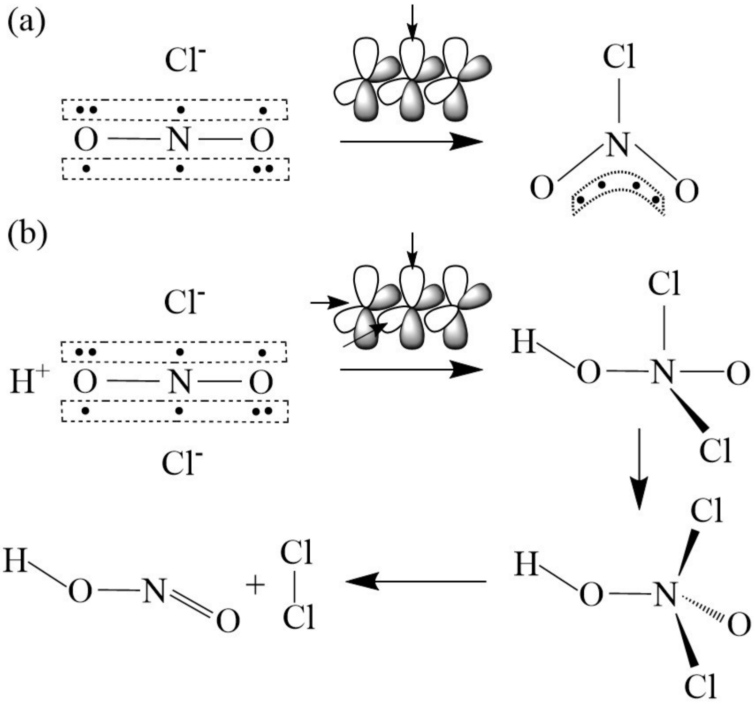
Response: we agree with the referee that other unconstrained factors, in addition to those examined, may influence the $\gamma(ClNO_2)$. We have now examined the dependence of $\gamma(ClNO_2)$ on RH, T, and other relevant aerosol components (e.g., NO_3^-, SO_4^{2-}, NH_4^+, and aerosol organics). Results show no obvious dependence of $\gamma(ClNO_2)$ on those parameters. We have clarified this point as follows.

Revision in the main text:

Line 398-400 (section 3.4.1): In our study, the D_p was derived from the ratio of wet V_a to S_a by assuming volume-limited uptake (Ammann et al., 2013). We also calculated D_p assuming surface-limited uptake, and no correlation with $\gamma(ClNO_2)_{obs}$ was indicated. Moreover, the $\gamma(ClNO_2)_{obs}$ showed no obvious relationship with other factors such as T, RH, aerosol liquid water content (ALW), NO_3^-, SO_4^{2-}, NH_4^+, and aerosol organics (figure not shown).

The authors propose that Cl2 formation is a co-product of ClNO2 when N2O5 is hydrolyzed on an acidic particle. I would like to see a bit more discussion of this potential mechanism. For ClNO2 the mechanism is quite straightforward: NO2+ reacts with Cl- to form ClNO2. For Cl2 it does not seem so obvious to me how exactly NO2+ and Cl interact to form Cl2. If the authors have a mechanism in mind please explain or add the relevant reference(s). Otherwise, if this is simply an hypothesis, then please state so clearly.

Response: we agree it would make the contention much more convincing if we can suggest the potential formation mechanism for Cl_2 from reaction of Cl^- and NO_2^+. Here is our proposed mechanism (see below figure). According to the hybrid orbital theory, the NO_2^+ ion has two non-bonded π molecular orbitals due to participation of the d orbital of the central nitrogen atom (Baird et al., 1981). When Cl^- attacks one of the π molecular orbitals, $ClNO_2$ is formed. In the same way, Cl^- can attach to the other π molecular orbitals of NO_2^+ and form a short-lived HNO_2Cl_2 intermediate in presence of H^+. Then, HNO_2Cl_2 decomposes to produce HONO and Cl_2.



Revision in the main text:

Line 402-404 (section 3.4.1): The mechanism is depicted in Figure 7 and goes as follows. It is known that N_2O_5 hydrolysis on aerosol is responsible for the production of NO_2^+. According to the hybrid orbital theory, the NO_2^+ ion has two non-bonded π molecular orbitals due to participation of the d orbital of the central nitrogen atom (Baird and Tayler, 1981). $ClNO_2$ is formed via the nucleophilic addition of Cl^- to one of the π molecular orbitals of NO_2^+ (Figure 7a) (Taylor, 1990; Behnke et al., 1997). In the same way, we propose a side reaction that the second Cl^- can attach to the other π molecular orbital of NO_2^+ and form a short-lived HNO_2Cl_2 intermediate in presence of H^+. It is proposed that the unstable HNO_2Cl_2 decomposes to produce Cl_2 (and HONO) (Figure 7b). This mechanism can explain concurrent productions of Cl_2 and $ClNO_2$ from N_2O_5 hydrolysis but needs confirmation by additional laboratory and theoretical studies.

Minor Comments ————

Section 2.1: Are there other relevant parameters (e.g., NOx) that you can use to compare the two sampling sites?

Response: it is a pity that only simultaneous measurements of O_3 were conducted at both sites.

Section 2.2: Can you please add the detection limits to the text? It would also be useful to see examples of spectra for N2O5, ClNO2, Cl2 and HOCl (these could go in the Supplementary Information).

Response: agreed. We have added the detection limits of N_2O_5, $ClNO_2$, and Cl_2 in the main text, and an example of spectra in the supplementary information. Below is the revision.

Revision in the main text:

Line 153-154 (section 2.2): The detection limits (3σ) of N_2O_5, $ClNO_2$, Cl_2 were 7 pptv, 2 pptv, and 5 pptv, respectively.

Revision in the SI:

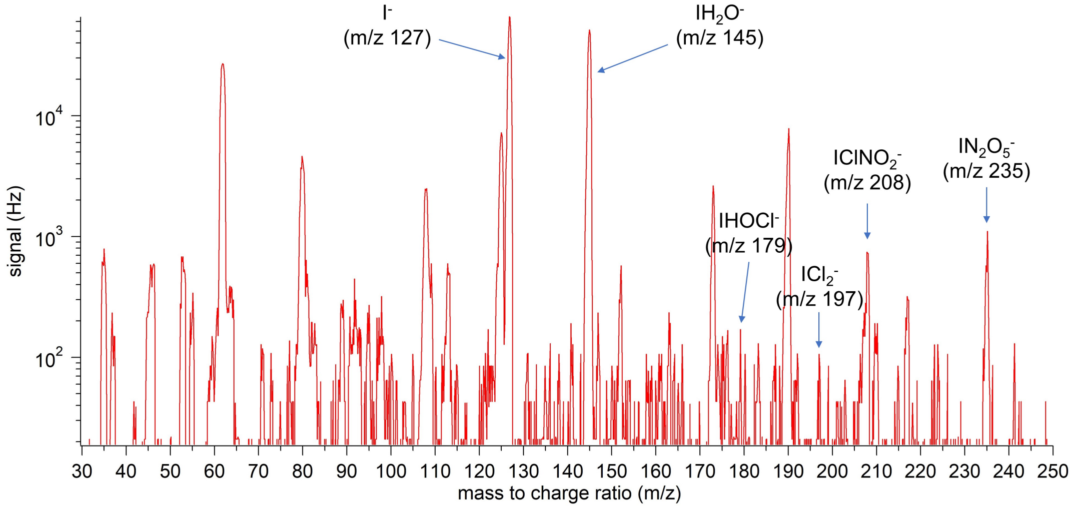


Figure S3. An example of the CIMS spectra taken at 18 April 01:00 LT.

Line 187: what about NO3 photolysis?

Response: thanks for the reminder of NO_3 photolysis, but in the present study, we focus on the nighttime chemistry of NO_3. So, the $k(NO_3)$ here is the loss rate for nighttime, and photolysis is not included.

Section 3.2: It seems to me, from figure 3, that the levels of VOC also play a role, not just O3, RH and Temperature.

Response: the role of VOCs had been included in the calculation the NO_3 reactivity which is dependent on VOC levels. For example, In the plume 3, the NO_3 reactivity due to VOCs decreased compared that in the plume 1. So, a larger proportion of NO_3 was lost via N_2O_5 uptake in the plume 3, which promoted $ClNO_2$ formation.

Lines 416-423: What about the outflow from Nanjing, which is west of the sampling site? I would think there are industrialized areas also on that part of the country not just between Nanjing and the ocean. Are SO2 and NOx very different in the two cases shown in figure 7? Can you please add some detail.

Response: 1. this is a good point. We have examined backward trajectories for the whole observation period but did not identify air masses from urban Nanjing in the west. Please see the figure below. We have added the trajectories figure in the SI.

Revision in the SI:

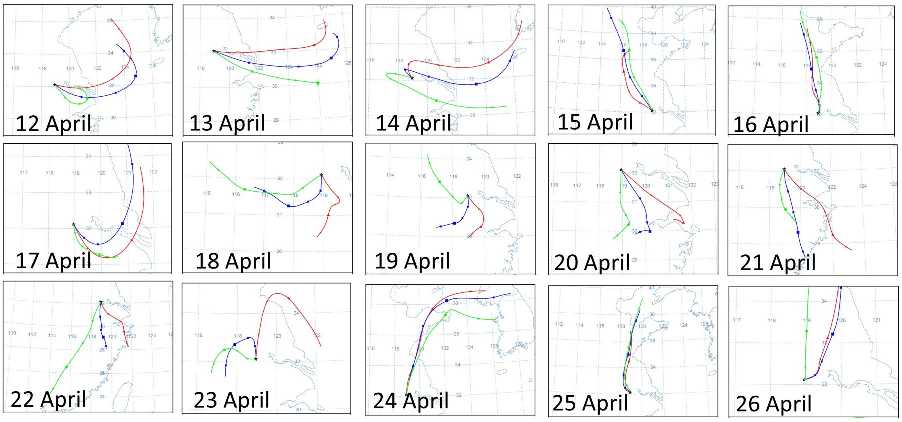


Figure S2. Daily backward trajectories arriving at the sampling sites during the field observation period.

2. The levels of NO_x and SO_2 are slightly higher in marine air compared with continental air in the two cases in figure 7 (see the table below). We have added this point in the main text.

Date	NO_x (ppb)	SO_2 (ppb)	Note
13-Apr	13.1±3.1	3.9±0.1	Marine air passing YRD industry
18-Apr	11.5±0.6	3.3±0.3	Continental air

Revision in the main text:
Line 420-422 (section 3.4.2): The average concentrations of SO_2 (3.9±0.1ppbv) and NO_x (13.1 ± 3.1 ppbv) in the marine air masses were higher than those (NO_x: 11.5±0.6 ppbv, SO_2: 3.3±0.3 ppbv) in the inland air masses.

Response to interactive comment on "Significant production of $ClNO_2$ and possible source of Cl_2 from N_2O_5 uptake at a suburban site in eastern China" by Men Xia et al. from anonymous Referee #2

General Comment

The paper entitled with "Significant production of ClNO2 and possible source of Cl2 from N2O5 uptake at a suburban site in eastern China" presented comprehensive observations of N2O5, ClNO2 and Cl2 as well as other supporting parameters at a regional site in Nanjing. The authors performed a detailed studies on the heterogeneous processes subjected to N2O5 uptake and the chlorine productions. Some insights are given on the multiphase chemistry production of Cl2. This study further extends the current exploration of the nighttime chemistry in China from North China Plain and Pearl River Delta to Yangtze River Delta which are certainly valuable to be published in ACP. Nevertheless, I think the current analysis needs some further careful check especially for the Section 3.4 as suggested in the follows.

Response: we appreciate the reviewer for the positive comments and helpful suggestions. Below is the response to each comment. The reviewers' comments are italicized, followed by our responses and changes shown in blue and red, respectively. And the corrections are also marked as red color in the revised manuscript. Please note that the line numbers mentioned below refer to the original submission (line numbers in the revised version have changed).

Specific Comment

1. Line 149 – 150. More details need to be given for the sentence "the permeation rate of Cl2 was quantified by chemical titration and ultraviolet spectrophotometry." How much Cl2 is generated for calibration and what is the accuracy?

Response: we have added more details of Cl_2 calibration. The permeation rate of Cl_2 generated for calibration is 380 ± 20 ng/min. We have added further details of Cl_2 calibration in the SI. Below is the revision.

Revision in the SI:

Text S1.4. Details of Cl_2 calibration

The Cl_2 standard was generated from a permeation tube heated to 40 °C and flushed by ultrapure nitrogen gas (20 sccm) and then diluted in humidified zero air (6 SLPM). During the field campaign, Cl_2 from the permeation tube was introduced into a KI solution (2% wt) for 1 hour. The permeation rate of Cl_2 (380 ± 20 ng/min) was calculated from the I_3^- concentration in the KI solution which was measured by ultraviolet–visible spectrophotometry at 351 nm.

2. Section 3.2. The high ClNO2 case is of high interest. It would be nice if the authors can try to analyze why the ClNO2 production become higher for plume 3 than plume1. The Cl- ion concentrations seem to be quite small and constant for the whole period.

Response: we did analyze the reason for the higher $ClNO_2$ production in the plume 3. As shown in lines 273-277 and Fig. 3, larger proportion of NO_3 was lost via N_2O_5 uptake in plume 3, which caused elevated $ClNO_2$ production in plume 3 compared with plume 1. As the Cl^- concentration was similar in plumes 1 and 3 (0.17 ± 0.02 and 0.19 ± 0.03 μg/m^3, respectively), we did not attribute the higher $ClNO_2$ in plume 3 to Cl^- concentrations.

Low chloride concentrations while high levels of $ClNO_2$ were also observed in previous studies, where HCl condensation was proposed to replenish particulate chloride to sustain the $ClNO_2$ production (Osthoff et al., 2008; Thornton et al., 2010). We have clarified this point in the revised manuscript.

Revision in the main text:

Line 277-278 (section 3.2): Compared with the high levels of $ClNO_2$ (up to 3.5 ppbv) on the night of 17 April, the concentration of Cl^- was low and relatively constant (~0.1 ppbv) during that period. The low chloride but high $ClNO_2$ levels were also observed in previous studies, and HCl partition was proposed to replenish particulate chloride to sustain the $ClNO_2$ production (Osthoff et al., 2008; Thornton et al., 2010).

3. Line 306-307. "The φ(ClNO2) value ranged from 0.28 to 0.89 (mean, 0.56 _ 0.15), which was among the highest values in the world (McDuffie et al., 2018b)." I suggest to delete "which was among the highest values in the world (McDuffie et al., 2018b)." The φ(ClNO2) is varied within 0-1 depending on the ratio of [Cl-]/[H2O], so I do not think the highest is meaningful.

Response: we agree and will delete “which was among the highest values in the world”.

4. Line 338. The equation 11 and corresponding text. I think the estimation and the use of [org] needs more discussion. If the reaction between org and NO2+ is the key to formulate the equation, then the org should be the part of water soluble organics. And I wonder why the reaction with acetate can be similar to the field observations presented herein. What are the major water soluble organics here in this study? And actually you have two adjustable parameters, one is k5 and the other is the exact [org].

Response: we agree that ideally the [org] here should be water-soluble organics. However, the water-soluble organics are not available in our study, and only total organics were measured on-site. So operationally we assume that organics are all water-soluble, similar to previous studies (McDuffie et al., 2018a; McDuffie et al., 2018b).

The k_5/k_3 value derived here (2.06) happens to be similar to that of acetate. One possibility is that the aerosol organics have a weighted average k_5/k_3 value of 2.06. Due to limited observation species, we don’t know the exact composition of water-soluble organics.

k_5 is the only adjustable parameter here. Since we assumed all observed aerosol organics to be water-soluble, the unknown water-soluble proportion of organics is factored in k_5.

Revision in the main text:

Line 331-334 (section 3.3) Here we assumed that the observed aerosol organics were all water-soluble and reactive toward NO_2^+, as previous studies did (McDuffie et al., 2018a; McDuffie et al., 2018b). The unknown water-soluble proportion of aerosol organics is factored in k_5.

Line 350-352 (section 3.3): A recent laboratory study (Staudt et al., 2019) derived $k_5/k_3 = 3.7$ for acetate, which happens to be very similar to our results.

5. Line 375-376. The Dp is derived from the ratio of the wet Va to Sa. As I understood, the the dry Dp is measured directly from SMPS instrument and the wet Dp can be estimated from empirical GF factor or measurements if available. It may be worth to check two kinds of Dp for your calculations, one is for the surface area concentrations when it is surface limited, and the other is for the volume concentrations when it is limited by volume bulk reactions. The calculation of the Gamma_ClNO2 may be influenced by the choice of the different Dp. A slightly different equation is suggested for your test of the gamma_ClNO2.

K_het = 1 / (Dp/Dg + 4/(gamma_ClNO2*c_ClNO2)) * 3 * ALW/Dp

Dg, gas diffusion constant

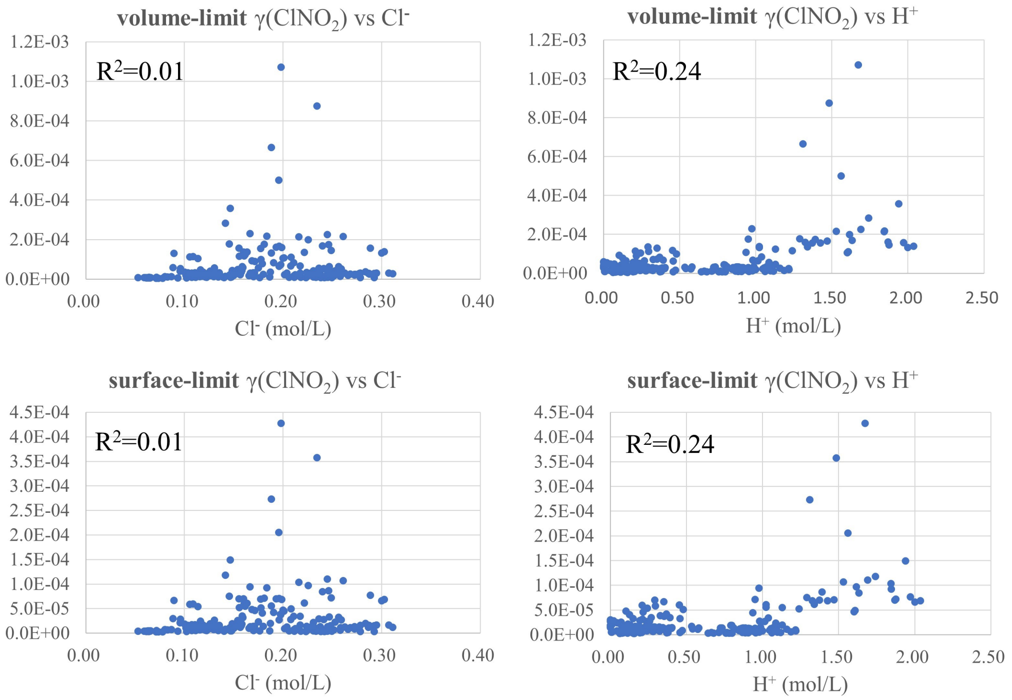
ALW, aerosol liquid water content

Response: we calculated D_p from the V_a/S_a ratio (255.3±32.9 nm in campaign average) based on the volume-limited uptake, we now also calculate D_p according to the average surface area of aerosols, which represents the surface-limited uptake. The surface-limited D_p gives a result of 122.6±26.7 nm in campaign average. The $\gamma(ClNO_2)$ is independent of both the surface-limited D_p and volume-limited D_p.

We appreciate the referee for suggesting a formula to test the $\gamma(ClNO_2)$. After investigating this formula, we suggest that D_p should be replaced with R_p (particle radius) before using this formula. Then, we adopt both volume-limited D_p and surface-limited D_p in this formula and derive $\gamma(ClNO_2)$, respectively. Results are shown in the table below.

Statistics	$\gamma(ClNO_2)$ in our paper	volume-limited $\gamma(ClNO_2)$	surface-limited $\gamma(ClNO_2)$
average value	1.1E-04	6.8E-05	3.1E-05
standard deviation	2.0E-04	1.2E-04	5.1E-05

Then, we investigate the relationship between $\gamma(ClNO_2)$ (volume-limited and surface-limited, respectively) and Cl^- and H^+. While no significant correlation is indicated. Results are shown in the figure below.



To sum, we will state in the manuscript that we examine the relationship between $\gamma(ClNO_2)$ and D_p derived from both volume-limited uptake and surface-limited uptake. Since different methods of calculating $\gamma(ClNO_2)$ lead to the same conclusion, i.e., no correlation between $\gamma(ClNO_2)$ and Cl^- and H^+, we prefer sticking to our original method to derive $\gamma(ClNO_2)$.

Revision in the main text:
Line 398-400 (section 3.4.1): In our study, the D_p was derived from the ratio of wet V_a to S_a by assuming volume-limited uptake (Ammann et al., 2013). We also calculated D_p assuming surface-limited uptake (diameter of the average surface area), and no correlation with $\gamma(ClNO_2)_{obs}$ was indicated.

6. Line 397 – 400. The ALW could be a variable to check for Cl2 production.
Response: thanks for this suggestion. we have checked ALW in Cl_2 production by investigating the dependence of $\gamma(ClNO_2)$ on ALW. However, no obvious correlation is found. We have clarified this point.
Revision in the main text:
Line 398-400 (section 3.4.1): …Moreover, the $\gamma(ClNO_2)_{obs}$ showed no obvious relationship with other factors such as T, RH, **aerosol liquid water content (ALW)**, NO_3^-, SO_4^{2-}, NH_4^+, and

aerosol organics (figure not shown).

7. Section 3.4.1 and 3.4.2, if the essence of Cl2 production is from ClNO2(aq) + H+ + Cl- → Cl2(g) Both the production of ClNO2 uptake and N2O5 uptake which can generate ClNO2(aq) could be the explanation for the Cl2 production. The authors may then to quantify the ratio of these two channels from the observations. In addition, the HOCl channel can also be assessed.

Response: we think both $ClNO_2$ uptake and direct N_2O_5 uptake can generate $ClNO_2$(aq) and then produce Cl_2. However, based on ambient measurements, we cannot separate the contribution of the two pathways, because an assumption to derive $\gamma(ClNO_2)$ was that Cl_2 was all produced by $ClNO_2$ uptake (Eq. 13, line 369). We will clarify in the revised draft that N_2O_5 uptake and $ClNO_2$ uptake are indistinguishable in driving Cl_2 production.

Since HOCl and Cl_2 were poorly correlated, we believe that the HOCl channel has minor contributions to Cl_2 production at our site.

Revision regarding this comment is made together with the comment 8.

8. Section 3.4.2, the analysis of phi(ClNO2) is only meaningful, if the authors can prove the N2O5 uptake is the major (i.e. >90%) production channel of the Cl2.

Response: we think that the referee meant $\varphi(Cl_2)$ in the above comment. In this paper, we attempt to demonstrate/argue that the three previously proposed reaction pathways could not explain the observed Cl_2 productions at night at our site, and suggest an additional one. We summarize our views as follows.

1. For $ClNO_2$→Cl_2, in section 3.4.1, we showed that the $\gamma(ClNO_2)$ derived from the assumption that Cl_2 was from $ClNO_2$ uptake didn't have the expected relationships with Cl^-, H^+, and D_p, which are the known factors that influence the $ClNO_2$ uptake. Thus, we argue that it could not be the main pathway for Cl_2 production at our site. We note that for our proposed new Cl_2 pathway: $NO_2^+ + Cl^- + H^+$, we do not rule out the $ClNO_2$ uptake channel, but assume it can produce Cl_2 via NO_2^+.

2. For HOCl→Cl_2, we think it is a minor Cl_2 production channel, because Cl_2 was not correlated to HOCl but highly correlated with $ClNO_2$ during most nights. The same logic was adopted in a previous study (Haskins et al., 2019) to support the view of insignificant role of HOCl.

3. For $ClONO_2$→Cl_2, $ClONO_2$ were not measured in our study. According to a recent field study in north China, nocturnal $ClONO_2$ levels was low (maximum~15 pptv). So, we assume that $ClONO_2$→Cl_2 was not a significant Cl_2 formation pathway, given the $\gamma(ClONO_2)$ on the order of 10^{-3} (Burkholder et al., 2015).

Revision for comments 7 and 8 in the main text:

Line 348-352 (section 3.4.1)

Our result suggests that Cl_2 was related to $ClNO_2$, but the HOCl pathway (R5) and coal burning were of minor importance at our site. $ClONO_2$ was not measured during our study. Recent field measurements at a rural site in northern China reported low $ClONO_2$ levels at night (maximum ~ 15 pptv) (Breton et al., 2018). We believe that the $ClONO_2$ levels at our site was also low, and production pathway (R6) was insignificant given low $\gamma(ClONO_2)$ (~10^{-3}) (Haskins et al., 2019). At our site, the $Cl_2/ClNO_2$ ratios varied on different nights, which implies that differences exist in the production efficiencies of Cl_2 relative to those of $ClNO_2$.

Line 381-383 (section 3.4.1)

For example, the box for 18:00–19:00 contains the $\gamma(ClNO_2)$ estimated at 18:00–19:00 on 11, 12, and 14 April (Fig. 6b–6d, orange lines). Fig. 6b–6d displays the observed Cl_2 levels (blue lines) and the projected trends of Cl_2 levels from Eq. (12), where the grey lines adopted the highest $\gamma(ClNO_2)$ value, 6.69×10^{-5} observed in the field study of Haskins et al. (2019). During early evening hours (i.e., 18:00–19:00), the $\gamma(ClNO_2)$ value derived in our study was one to two orders of magnitude higher than those in that study. This result implies that either $ClNO_2$ uptake was much faster at our site or other pathways were involved in Cl_2 production. We provide evidence below that the latter is likely the case.

Line 406-411 (section 3.4.1)

We propose a new framework to estimate nighttime Cl_2 production by treating Cl_2, $ClNO_2$, and most nitrate all ultimately originating from N_2O_5 uptake. We assign a production yield to Cl_2 from the N_2O_5 uptake ($\varphi(Cl_2)$) analogous to the $ClNO_2$ yield and calculate this metric using Eq. (14):

$$\varphi(Cl_2) = \frac{d[Cl_2]/dt}{k(N_2O_5)[N_2O_5]} \tag{14}$$

The above formulation does not rule out the production of Cl_2 from the $ClNO_2$ uptake, because such production, if any, is also a result of N_2O_5 uptake and has thus been incorporated in Eq. (14).

Reference:

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