

Response to interactive comment on “Significant production of ClNO₂ and possible source of Cl₂ from N₂O₅ 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 has 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 Cl₂ calibration. The permeation rate of Cl₂ generated for calibration is 380 ± 20 ng/min. We have added further details of Cl₂ calibration in the SI. Below is the revision.

Revision in the SI:

Text S1.4. Details of Cl₂ calibration

The Cl₂ 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, Cl₂ from the permeation tube was introduced into a KI solution (2% wt) for 1 hour. The permeation rate of Cl₂ (380 ± 20 ng/min) was calculated from the I₃⁻ 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 ClNO₂ production in the plume 3. As shown in lines 273-277 and Fig. 3, larger proportion of NO₃ was lost via N₂O₅ uptake in plume 3, which caused elevated ClNO₂ 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/m³, respectively), we did not attribute the higher ClNO₂ in plume 3 to Cl⁻ concentrations.

Low chloride concentrations while high levels of ClNO₂ were also observed in previous studies, where HCl condensation was proposed to replenish particulate chloride to sustain the ClNO₂ 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 ClNO₂ (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 ClNO₂ levels were also observed in previous studies, and HCl partition was proposed to replenish particulate chloride to sustain the ClNO₂ production (Osthoff et al., 2008; Thornton et al., 2010).

3. Line 306-307. “The $\phi(\text{ClNO}_2)$ value ranged from 0.28 to 0.89 (mean, 0.56 \pm 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 $\phi(\text{ClNO}_2)$ is varied within 0-1 depending on the ratio of $[\text{Cl}^-]/[\text{H}_2\text{O}]$, 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 k_5 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 NO₂⁺, 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 D_p is derived from the ratio of the wet V_a to S_a. As I understood, the the dry D_p is measured directly from SMPS instrument and the wet D_p can be estimated from empirical GF factor or measurements if available. It may be worth to check two kinds of D_p 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 γ_{ClNO_2} may be influenced by the choice of the different D_p . A slightly different equation is suggested for your test of the γ_{ClNO_2} .

$$K_{\text{het}} = 1 / (D_p/D_g + 4/(\gamma_{\text{ClNO}_2} \cdot c_{\text{ClNO}_2}) * 3 * ALW/D_p)$$

D_g , gas diffusion constant

ALW , aerosol liquid water content

Response: we calculated D_p (127.6±16.5 nm) based on the volume-limited uptake, we now also calculated D_p based on the surface-limited uptake which gives a similar result (122.6±26.7 nm). The $\gamma(\text{ClNO}_2)$ 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 $\gamma(\text{ClNO}_2)$. We could not find the origin of this formula in literature, and it is not clear to us how we can use this formula to derive $\gamma(\text{ClNO}_2)$ from ambient measurements. In our study, we use below Eq. 13 to calculate $\gamma(\text{ClNO}_2)$, which does not involve D_p , thus the calculation of $\gamma(\text{ClNO}_2)$ was not influenced by the choice of D_p .

$$\gamma(\text{ClNO}_2)_{\text{obs}} = \frac{4d[\text{Cl}_2]/dt}{c(\text{ClNO}_2)S_a[\text{ClNO}_2]} \quad (13)$$

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 obtained similar D_p values to the volume-limited approach, and no correlation with $\gamma(\text{ClNO}_2)_{\text{obs}}$ was indicated.

6. Line 397 – 400. The ALW could be a variable to check for Cl_2 production.

Response: thanks for this suggestion. we have checked ALW in Cl_2 production by investigating the dependence of $\gamma(\text{ClNO}_2)$ on $[\text{H}_2\text{O}]$. 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 $\gamma(\text{ClNO}_2)_{\text{obs}}$ showed no obvious relationship with other factors such as T , RH , H_2O , 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 Cl_2 production is from $\text{ClNO}_2(\text{aq}) + \text{H}^+ + \text{Cl}^- \rightarrow \text{Cl}_2(\text{g})$ Both the production of ClNO_2 uptake and N_2O_5 uptake which can generate $\text{ClNO}_2(\text{aq})$ could be the explanation for the Cl_2 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 $\text{ClNO}_2(\text{aq})$ and then produce Cl_2 . However, based on ambient measurements, we cannot separate the contribution of the two pathways, because an assumption to derive $\gamma(\text{ClNO}_2)$ 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 $\phi(\text{ClNO}_2)$ 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 $\phi(\text{Cl}_2)$ in the above comment. In this paper, we attempt to demonstrate/argue that the three previously proposed reaction pathways could not explain the observed Cl₂ productions at night at our site, and suggest an additional one. We summarize our views as follows.

1. For $\text{ClNO}_2 \rightarrow \text{Cl}_2$, in section 3.4.1, we showed that the $\gamma(\text{ClNO}_2)$ derived from the assumption that Cl₂ was from ClNO₂ uptake didn't have the expected relationships with Cl⁻, H⁺, and D_p, which are the known factors that influence the ClNO₂ uptake. Thus, we argue that it could not be the main pathway for Cl₂ production at our site. We note that for our proposed new Cl₂ pathway: $\text{NO}_2^+ + \text{Cl}^- + \text{H}^+$, we do not rule out the ClNO₂ uptake channel, but assume it can produce Cl₂ via NO₂⁺.

2. For $\text{HOCl} \rightarrow \text{Cl}_2$, we think it is a minor Cl₂ production channel, because Cl₂ was not correlated to HOCl but highly correlated with ClNO₂ 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 $\text{ClONO}_2 \rightarrow \text{Cl}_2$, ClONO₂ were not measured in our study. According to a recent field study in north China, nocturnal ClONO₂ levels was low (maximum~15 pptv). So, we assume that $\text{ClONO}_2 \rightarrow \text{Cl}_2$ was not a significant Cl₂ formation pathway, given the $\gamma(\text{ClONO}_2)$ 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 Cl₂ was related to ClNO₂, but the HOCl pathway (R5) and coal burning were of minor importance at our site. ClONO₂ was not measured during our study. Recent field measurements at a rural site in northern China reported low ClONO₂ levels at night (maximum ~ 15 pptv) (Breton et al., 2018). We believe that the ClONO₂ levels at our site was also low, and production pathway (R6) was insignificant given low $\gamma(\text{ClONO}_2)$ (~10⁻³) (Haskins et al., 2019). At our site, the Cl₂/ClNO₂ ratios varied on different nights, which implies that differences exist in the production efficiencies of Cl₂ relative to those of ClNO₂.

Line 381-383 (section 3.4.1)

For example, the box for 18:00–19:00 contains the $\gamma(\text{ClNO}_2)$ estimated at 18:00–19:00 on 11, 12, and 14 April (Fig. 6b–6d, orange lines). Fig. 6b–6d displays the observed Cl₂ levels (blue lines) and the projected trends of Cl₂ levels from Eq. (12), where the grey lines adopted the highest $\gamma(\text{ClNO}_2)$ 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 $\gamma(\text{ClNO}_2)$ value derived in our study was one to two orders of magnitude higher than those in that study. This result implies that either ClNO₂ uptake was much faster at our site or other pathways were involved in Cl₂ 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 Cl₂ production by treating Cl₂, ClNO₂,

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 ($\varphi(\text{Cl}_2)$) analogous to the ClNO_2 yield and calculate this metric using Eq. (14):

$$\varphi(\text{Cl}_2) = \frac{d[\text{Cl}_2]/dt}{k(\text{N}_2\text{O}_5)[\text{N}_2\text{O}_5]} \quad (14)$$

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).

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