Atmos. Chem. Phys. Discuss.,
https://doi.org/10.5194/acp-2019-1130-AC2, 2020

Atmospheric Chemistry and Physics Discussions

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.

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Received and published: 20 March 2020

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). Please refer to the supplement of this author comment for better views such as font color, subscripts, formulas, and so on.

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 âĎČ 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

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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 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 k5/k3 value derived here (2.06) happens to be similar to that of acetate. One possibility is that the aerosol organics have a weighted average k5/k3 value of 2.06. Due to limited observation species, we don't know the exact composition of water-soluble organics. k5 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 k5.

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 k5. Line 350-352 (section 3.3): A recent laboratory study (Staudt et al., 2019) derived k5/k3 = 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 Dp (127.6±16.5 nm) based on the volume-limited uptake, we now also calculated Dp based on the surface-limited uptake which gives a similar result (122.6±26.7 nm). The γ(ClNO2) is independent of both the surface-limited Dp and volume-limited Dp. We appreciate the referee for suggesting a formula to test the

γ(ClNO2). 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 γ(ClNO2) from ambient measurements. In our study, we use below Eq. 13 to calculate γ(ClNO2), which does not involve Dp, thus the calculation of γ(ClNO2) was not influenced by the choice of Dp. γ(ClNO2)obs = "4d[Cl2]/dt" /"c(ClNO2)Sa[ClNO2]" (13)

Revision in the main text: Line 398-400 (section 3.4.1): In our study, the Dp was derived from the ratio of wet Va to Sa by assuming volume-limited uptake (Ammann et al., 2013). We also calculated Dp assuming surface-limited uptake and obtained similar Dp values to the volume-limited approach, and no correlation with γ(ClNO2)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 Cl2 production by investigating the dependence of γ(ClNO2) on [H2O]. 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 γ(ClNO2)obs showed no obvious relationship with other factors such as T, RH, H2O, NO3-, SO42-, NH4+, 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 ClNO2 uptake and direct N2O5 uptake can generate ClNO2(aq) and then produce Cl2. However, based on ambient measurements, we cannot separate the contribution of the two pathways, because an assumption to derive γ(ClNO2) was that Cl2 was all produced by ClNO2 uptake (Eq. 13, line 369). We will clarify in the revised draft that N2O5 uptake and ClNO2 uptake are indistinguishable in driving Cl2 production. Since HOCl and Cl2 were poorly correlated, we believe that the HOCl channel has minor contributions to Cl2 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 φ(Cl2) 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 ClNO2→Cl2, in section 3.4.1, we showed that the γ(ClNO2) derived from the assumption that Cl2 was from ClNO2 uptake didn't have the expected relationships with Cl-, H+, and Dp, 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: NO2+ + Cl- + H+, we do not rule out the ClNO2 uptake channel, but assume it can produce Cl2 via NO2+. 2. For HOCl→Cl2, 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 ClONO2→Cl2, ClONO2 were not measured in our study. According to a recent field study in north China, nocturnal ClONO2 levels was low (maximum$\sim$15 pptv). So, we assume that ClONO2→Cl2 was not a significant Cl2 formation pathway, given the γ(ClONO2) 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 $\sim$ 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

γ(ClONO2) ($\sim$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 γ(ClNO2) 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 γ(ClNO2) value, 6.69$\times$10-5 observed in the field study of Haskins et al. (2019). During early evening hours (i.e., 18:00–19:00), the γ(ClNO2) 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 N2O5 uptake. We assign a production yield to Cl2 from the N2O5 uptake (φ(Cl2)) analogous to the ClNO2 yield and calculate this metric using Eq. (14): φ(Cl2) = ("d" ãĂŰ"[Cl" ãĂŮ_"2" "]/dt")/("k(" "N" _"2" "O" _"5")["N" _"2" "O" _"5"]) (14) The above formulation does not rule out the production of Cl2 from the ClNO2 uptake, because such production, if any, is also a result of N2O5 uptake and has thus been incorporated in Eq. (14).

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Please also note the supplement to this comment:
https://www.atmos-chem-phys-discuss.net/acp-2019-1130/acp-2019-1130-AC2-supplement.pdf

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Interactive comment on Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2019-1130, 2020.