

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.

Anonymous Referee #2

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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

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in ACP. Nevertheless, I think the current analysis needs some further careful check especially for the Section 3.4 as suggested in the follows.

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?
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 plume 1. The Cl⁻ ion concentrations seem to be quite small and constant for the whole period.
3. Line 306-307. “The $\varphi(\text{ClNO}_2)$ 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 $\varphi(\text{ClNO}_2)$ 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.
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].
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 Gamma_{ClNO₂} may be influenced by

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the choice of the different D_p . A slightly different equation is suggested for your test of the γ_{ClNO_2} .

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

D_g , gas diffusion constant

ALW , aerosol liquid water content

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

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.

8. Section 3.4.2, the analysis of $\phi(\text{ClNO}_2)$ is only meaningful, if the authors can prove the N_2O_5 uptake is the major (i.e. >90%) production channel of the Cl_2 .

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