

## ***Interactive comment on “Significant production of ClNO<sub>2</sub> and possible source of Cl<sub>2</sub> from N<sub>2</sub>O<sub>5</sub> 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 ClNO<sub>2</sub> and possible source of Cl<sub>2</sub> from N<sub>2</sub>O<sub>5</sub> uptake at a suburban site in eastern China” presented comprehensive observations of N<sub>2</sub>O<sub>5</sub>, ClNO<sub>2</sub> and Cl<sub>2</sub> as well as other supporting parameters at a regional site in Nanjing. The authors performed a detailed studies on the heterogeneous processes subjected to N<sub>2</sub>O<sub>5</sub> uptake and the chlorine productions. Some insights are given on the multiphase chemistry production of Cl<sub>2</sub>. 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 Cl<sub>2</sub> was quantified by chemical titration and ultraviolet spectrophotometry.” How much Cl<sub>2</sub> is generated for calibration and what is the accuracy?
2. Section 3.2. The high ClNO<sub>2</sub> case is of high interest. It would be nice if the authors can try to analyze why the ClNO<sub>2</sub> production become higher for plume 3 than plume 1. The Cl<sup>-</sup> 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,  $0.56 \pm 0.15$ ), 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  $\varphi(\text{ClNO}_2)$  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 NO<sub>2</sub><sup>+</sup> 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<sub>5</sub> and the other is the exact [org].
5. Line 375-376. The D<sub>p</sub> is derived from the ratio of the wet V<sub>a</sub> to S<sub>a</sub>. As I understood, the the dry D<sub>p</sub> is measured directly from SMPS instrument and the wet D<sub>p</sub> can be estimated from empirical GF factor or measurements if available. It may be worth to check two kinds of D<sub>p</sub> 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<sub>ClNO<sub>2</sub></sub> 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  $\gamma_{\text{ClNO}_2}$ .

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

$D_g$ , gas diffusion constant

ALW, aerosol liquid water content

6. Line 397 – 400. The ALW could be a variable to check for  $\text{Cl}_2$  production.

7. Section 3.4.1 and 3.4.2, if the essence of  $\text{Cl}_2$  production is from  $\text{ClNO}_2(\text{aq}) + \text{H}^+ + \text{Cl}^- \rightarrow \text{Cl}_2(\text{g})$  Both the production of  $\text{ClNO}_2$  uptake and  $\text{N}_2\text{O}_5$  uptake which can generate  $\text{ClNO}_2(\text{aq})$  could be the explanation for the  $\text{Cl}_2$  production. The authors may then to quantify the ratio of these two channels from the observations. In addition, the  $\text{HOCl}$  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  $\text{N}_2\text{O}_5$  uptake is the major (i.e. >90%) production channel of the  $\text{Cl}_2$ .

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