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*Supplement of*

## **Chlorine oxidation of VOCs at a semi-rural site in Beijing: significant chlorine liberation from ClNO<sub>2</sub> and subsequent gas- and particle-phase Cl–VOC production**

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1 **Supplementary information for: Chlorine oxidation of VOCs at a semi-rural site in**  
2 **Beijing: Significant chlorine liberation from ClNO<sub>2</sub> and subsequent gas and particle**  
3 **phase Cl-VOC production**

4

5 **Steady state calculations**

6 In previous work (Bannan et al., 2015) we have shown that it is possible to calculate Cl atom  
7 concentrations, using a simple steady-state expression with the Cl atom production rate estimated from  
8 the observed loss rate of ClNO<sub>2</sub> and removal of Cl atoms via reaction with the VOC concentrations  
9 supplemented with data from the Boston tailpipe study (AQIRP, 1995) and LA VOC study (Fraser et al.,  
10 1997), i.e. missing VOC concentrations are estimated simply by using the ratio of measured VOCs and  
11 missing VOCs from these urban studies and measured VOC data in this study. The removal of Cl atoms  
12 via reaction with VOCs can then be determined using Eq. 1-3, and NIST kinetic data (Manion et al., 2014)

13 
$$-d[\textit{alkanes}]/dt = [X] \sum_i k_{X+\textit{alkane},i} [\textit{alkane},i] \quad (\text{Eq 1})$$

14 
$$-d[\textit{alkenes}]/dt = [X] \sum_i k_{X+\textit{alkene},i} [\textit{alkene},i] \quad (\text{Eq 2})$$

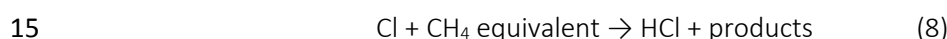
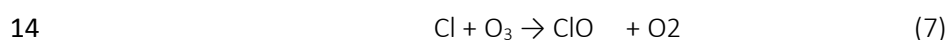
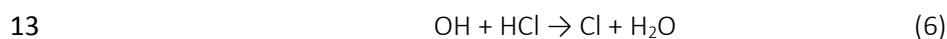
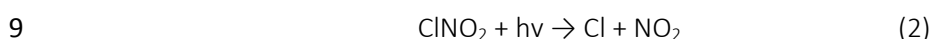
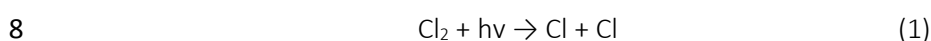
15 
$$-d[\textit{alkynes}]/dt = [X] \sum_i k_{X+\textit{alkyne},i} [\textit{alkyne},i] \quad (\text{Eq 3})$$

16 We were able to show that the simple state approach agreed well with a fully integrated chemical  
17 model using the MCM, despite a much more simplistic approach. We used an identical approach in this  
18 work utilizing the tailpipe VOC concentrations (AQIRP, 1995). However, we further simplify the  
19 approach by using one term CH<sub>4</sub> equivalent which accounts for relative concentration and reactivity  
20 towards Cl, i.e. if a VOC reacts 1000 times faster it is the equivalent of 1000 CH<sub>4</sub> or more formally for  
21 each VOC its CH<sub>4</sub> equivalent is  $k(\text{Cl} + \text{VOC}) [\text{VOC}] / k(\text{Cl} + \text{CH}_4)$ . Whilst the approach is a simplification of  
22 course, it has been shown that using these emissions it is possible to estimate the Cl atom production,  
23 albeit it with some significant error due to significant number of estimations made in a Megacity  
24 environment and produces results that are comparable with the much more thorough explicit  
25 modelling approach of the MCM. It also generates a metric, CH<sub>4</sub> equivalent, which can be used as a  
26 comparative measurement from city to city.

27 Photolysis rates were measured by a spectroradiometer for O<sub>3</sub>, NO<sub>2</sub>, HCHO, HONO and H<sub>2</sub>O<sub>2</sub>. The  
28 photolysis rate of any given species was calculated by normalizing to the cross section and quantum

1 yields taken from the recommendations of the Jet Propulsion Laboratory (JPL) kinetic evaluation report  
2 (Burkholder et al., 2015)."

3 "Consistent with past measurements and the measurements of this study, ClNO<sub>2</sub> is expected to provide  
4 a significant source of Cl during day time hours, presenting a potentially significant source of the  
5 reactive Cl atom during the day. Its rapid photolysis rate and elevated mixing ratios enables Cl to  
6 compete with OH oxidation chemistry, the known dominant daytime radical source. Here, a simple  
7 steady state calculation will be used to determine the Cl atom mixing ratio as detailed;



16 
$$[\text{Cl}]_{\text{SS}} = \{J_1[\text{Cl}_2] + J_2[\text{ClNO}_2] + J_3[\text{ClONO}_2] + J_4[\text{HOCl}] + J_5[\text{OCIO}] + k_7 [\text{OH}][\text{HCl}]\} / \{k_7[\text{O}_3] + k_8[\text{CH}_4]$$
  
17 
$$\text{equivalent}\} \quad (9)$$

18 Where [CH<sub>4</sub>] equivalent represents the reactive VOC present as if it were equivalent CH<sub>4</sub>

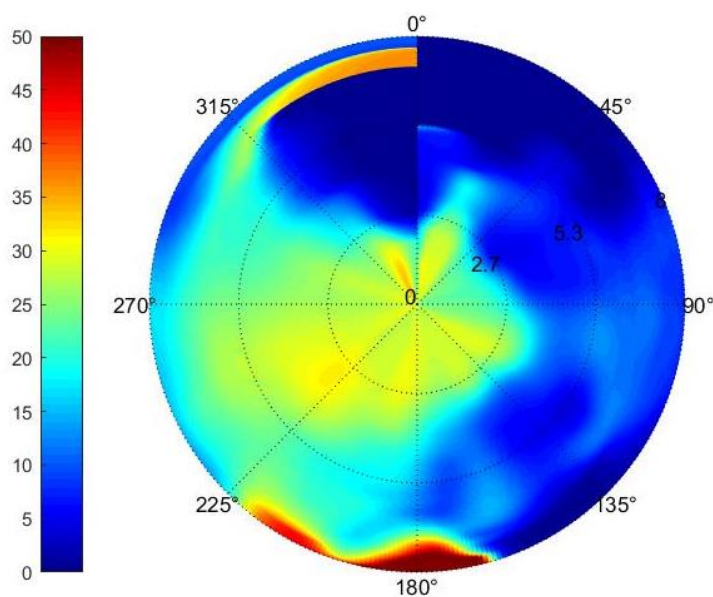
19 Bannan et al., (2005), were able to use this steady state approach to compare the relative loss via  
20 reaction with OH compared with Cl atoms. The total loss can be estimated using equations 1-3, using  
21 the steady state concentrations of Cl (estimated using equation 9) and a mean steady state OH  
22 calculated concentration of 7 x 10<sup>6</sup> molecules cm<sup>-3</sup>. Again, this approach is an estimation but was shown  
23 to produce comparable results with that of the more rigorous explicit model using the MCM. The main  
24 findings of this work, is that as we infer much higher concentrations of Cl atoms, as a result of much  
25 higher observed inorganic chlorine species, the impact of Cl atom chemistry is much higher than has  
26 been observed in previous work.

27 There is a large uncertainty in the radical concentrations estimated in this work using the steady state  
28 method and this is fully acknowledged. The production rates for Cl are calculated directly from

1 measurements of species, e.g. ClNO<sub>2</sub> concentrations and their photolysis rates, estimated by a  
2 photochemical model and so that aspect of the calculation has a relatively small uncertainty. There will  
3 be missing sources of Cl production that are not measured but the main known precursors are  
4 represented in these calculations. However, the loss rate carries the bulk of the uncertainty in these  
5 calculations; first it is known that not all VOCs are measured and even after estimation of missing VOCs  
6 there will be some missing loss. Second, calibration of some VOCs in this campaign will be uncertain,  
7 hence the reporting of counts per second rather than absolute numbers. Third, the rate coefficients  
8 associated with the loss processes will carry some uncertainty too. Finally, the distribution of missing  
9 VOCs is based on USA and European emission profiles and these maybe different from those from Asia.  
10 Therefore, the uncertainty in radical concentration using this method will be at least 50%, where 20%  
11 is from rate coefficient uncertainty, taking into consideration temperature dependences, and an  
12 estimated 30% from uncertainty in concentration measurements. However, OH reactivity  
13 measurements (e.g. Yang et al., 2016) provide a direct measurement of total loss rates and although  
14 not a direct comparison with Cl loss rates they can serve as a guide. Using 20s<sup>-1</sup> as an estimate for the  
15 total loss rate for OH the steady state calculations are predicting loss rates in the range 10-15 s<sup>-1</sup>.  
16 Therefore, a 50% uncertainty and recognising that the concentrations generated are almost certainly  
17 an upper limit provides some further context to these calculations.

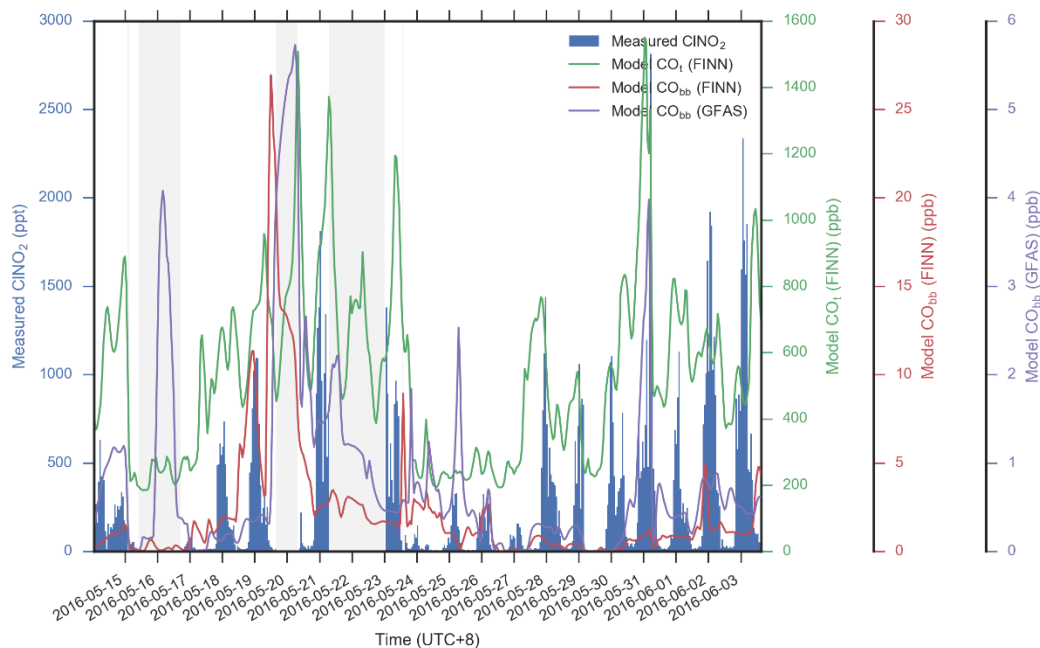
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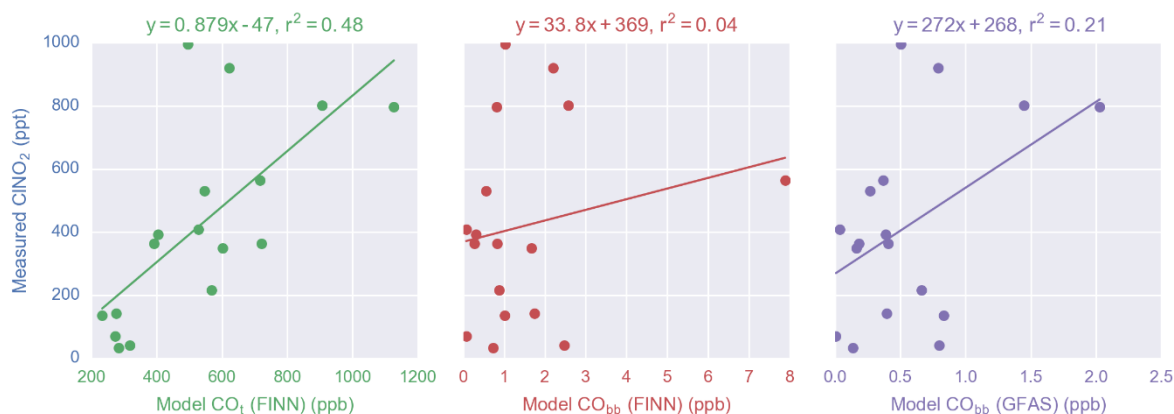
20

21 **Figure S1. Wind rose during the campaign in Changping**



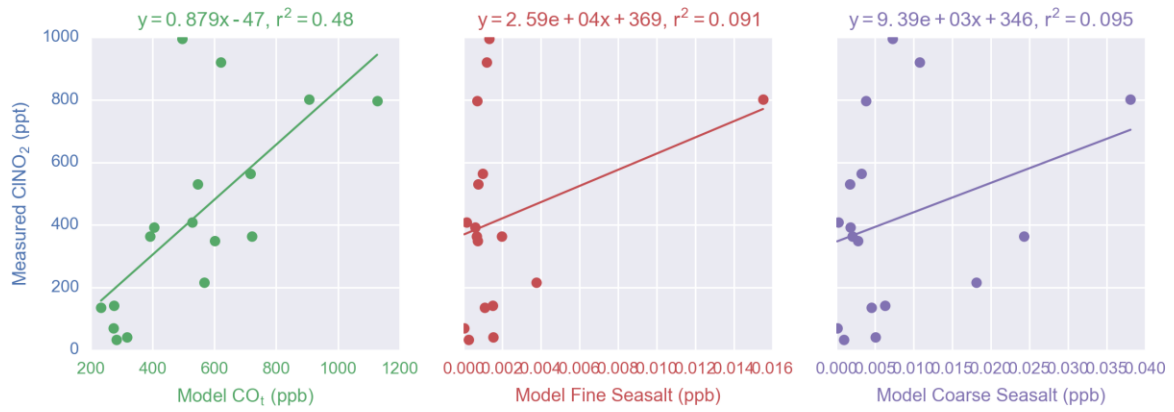
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2 **Figure S2. Time series of measured CINO<sub>2</sub> concentrations, modelled CO<sub>t</sub> concentrations,**  
 3 **and modelled CO<sub>bb</sub> at the Changping site. CO<sub>bb</sub> is shown for both the model using the**  
 4 **FINN database and the GFAS database. Periods with missing measurement data are**  
 5 **shown in grey.**



6

7 **Figure S3. Scatter plots of night-time averages of CINO<sub>2</sub> against corresponding averages**  
 8 **of CO<sub>t</sub>, CO<sub>bb</sub> in the FINN model, and CO<sub>bb</sub> in the GFAS model. Linear regressions for**  
 9 **each of the comparisons gave the following r<sup>2</sup> results: CO<sub>t</sub> 0.48, CO<sub>bb</sub> FINN 0.04, and**  
 10 **CO<sub>bb</sub> GFAS 0.21.**



1

2 **Figure S4. Correlation plots of measured ClNO<sub>2</sub> vs modelled CO<sub>t</sub> (green), fine seasalt**  
 3 **(red) and course seasalt (blue).**

4

- 5 1. Yang, Y., Shao, M., Wang, X., Nolscher, A.C., Kessel, S., Guether, A. and Williams, J.: Towards  
 6 a quantitative understanding of total OH reactivity: A review. *Atmos. Environ.*, **134**, 147-161  
 7 (2016).