

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

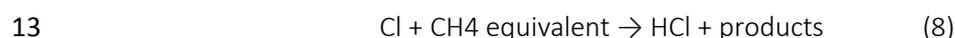
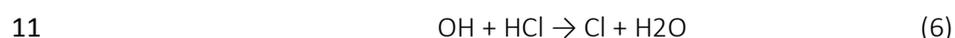
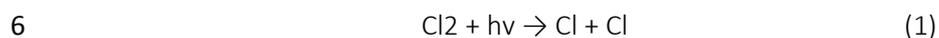
14 
$$-d[\textit{alkenes}]/dt = [X] \sum_i k_{X+\textit{alkene},i} [\textit{alkene},i] \quad (\text{Eq 2})$$

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

26 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  
27 photolysis rate of any given species was calculated by normalizing to the cross section and quantum  
28 yields taken from the recommendations of the Jet Propulsion Laboratory (JPL) kinetic evaluation report  
29 (Burkholder et al., 2015)."

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



14 
$$[\text{Cl}]_{\text{SS}} = \{J_1[\text{Cl}_2] + J_2[\text{ClNO}_2] + J_3[\text{ClONO}_2] + J_4[\text{HOCl}] + J_5[\text{OCIO}] + k_7 [\text{OH}][\text{HCl}]\} / \{k_7[\text{O}_3] + k_8[\text{CH}_4]$$
  
15 
$$\text{equivalent}\} \quad (9)$$

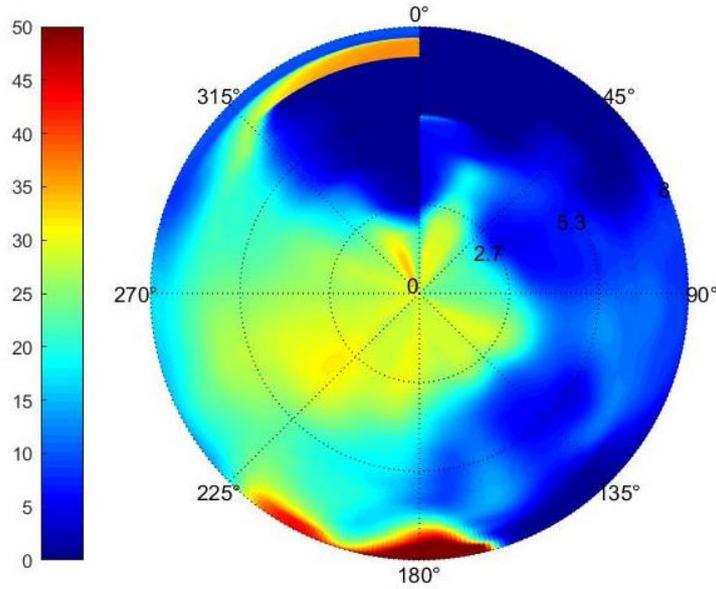
16 Where [CH<sub>4</sub>] equivalent represents the reactive VOC present as if it were equivalent CH<sub>4</sub>

17 Bannan et al., (2005), were able to use this steady state approach to compare the relative loss via  
18 reaction with OH compared with Cl atoms. The total loss can be estimated using equations 1-3, using  
19 the steady state concentrations of Cl (estimated using equation 9)

20 
$$[\text{Cl}]_{\text{SS}} = \{J_1[\text{Cl}_2] + J_2[\text{ClNO}_2] + J_3[\text{ClONO}_2] + J_4[\text{HOCl}] + J_5[\text{OCIO}] + k_7 [\text{OH}][\text{HCl}]\} / \{k_7[\text{O}_3] + k_8[\text{CH}_4]$$
  
21 
$$\text{equivalent}\} \quad (9)$$

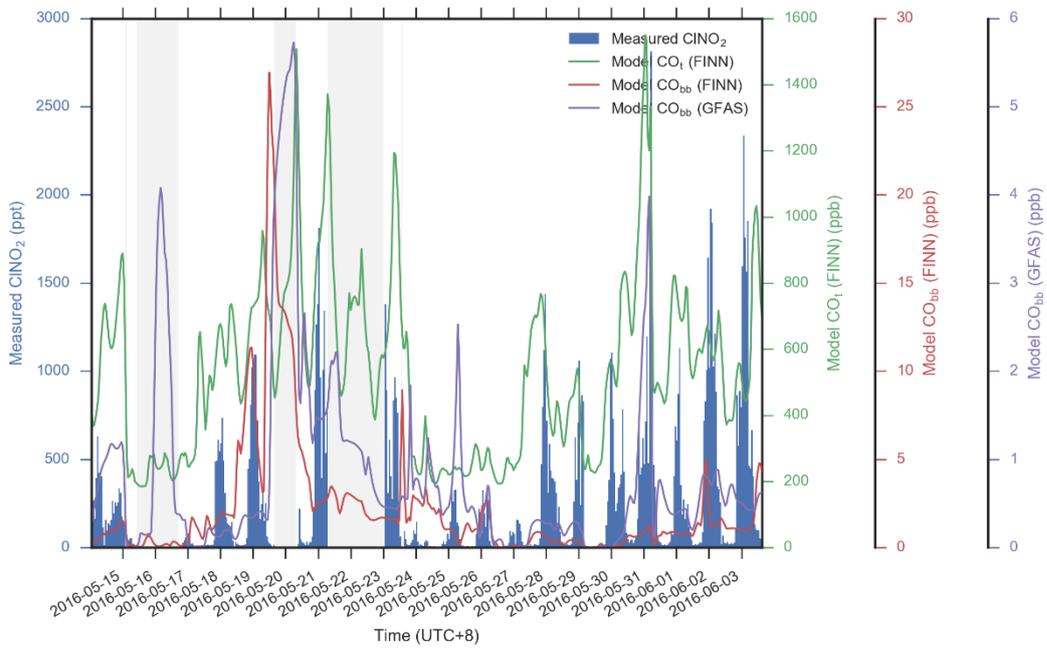
22 and a mean steady state OH calculated concentration of  $7 \times 10^6$  molecules cm<sup>3</sup>. Again, this approach  
23 is an estimation, but was shown to produce comparable to results with that of the more rigorous  
24 MCM approach. The main findings of this work, is that as we infer much higher concentrations of Cl  
25 atoms, as a result of much higher observed inorganic chlorine species, the impact of Cl atom  
26 chemistry is much higher than has been observed in previous work.

27



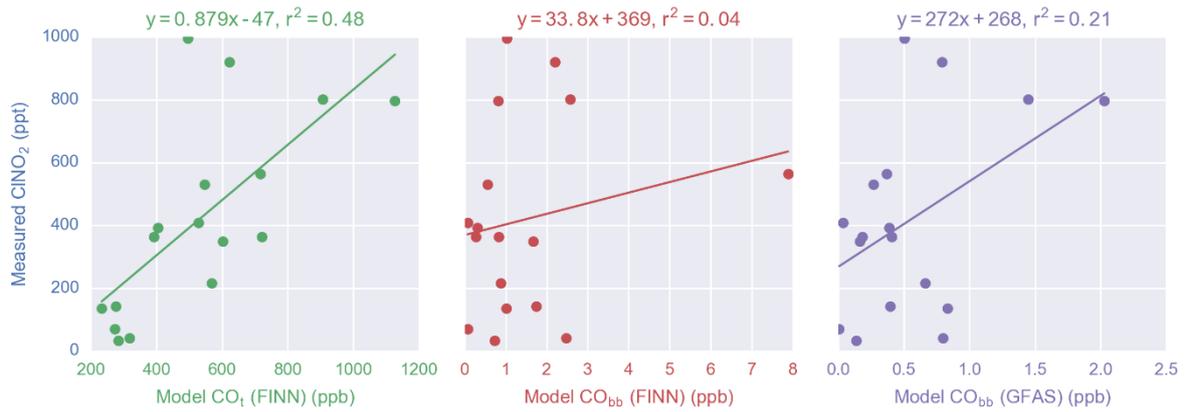
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2 **Figure S1. Wind rose during the campaign in Changping**



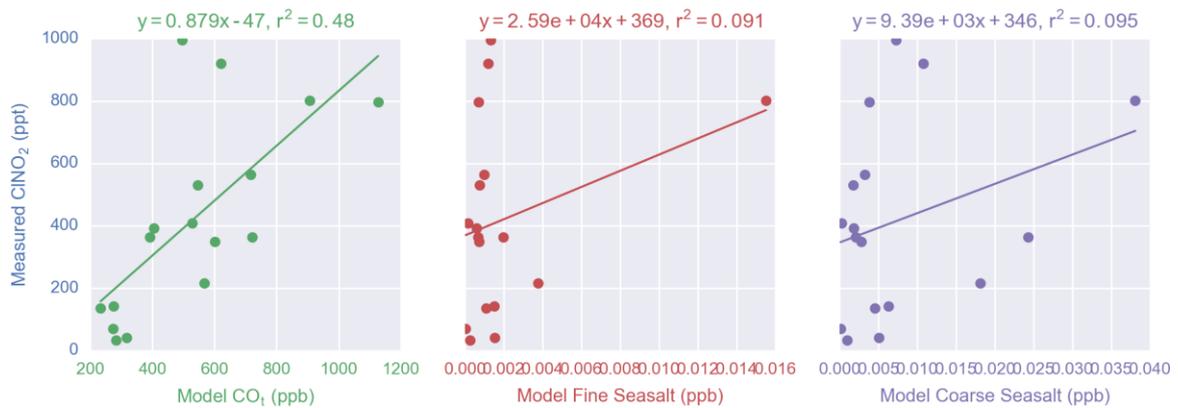
3

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



1

2 **Figure S3. Scatter plots of night-time averages of CINO<sub>2</sub> against corresponding averages**  
 3 **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**  
 4 **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**  
 5 **CO<sub>bb</sub> GFAS 0.21.**



6

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

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