Supplementary information for: Chlorine oxidation of VOCs at a semi-rural site in Beijing: Significant chlorine liberation from ClNO$_2$ and subsequent gas and particle phase Cl-VOC production

Steady state calculations

In previous work (Bannan et al., 2015) we have shown that it is possible to calculate Cl atom concentrations, using a simple steady-state expression with the Cl atom production rate estimated from the observed loss rate of ClNO$_2$ and removal of Cl atoms via reaction with the VOC concentrations supplemented with data from the Boston tailpipe study (AQIRP, 1995) and LA VOC study (Fraser et al., 1997), i.e. missing VOC concentrations are estimated simply by using the ratio of measured VOCs and missing VOCs from these urban studies and measured VOC data in this study. The removal of Cl atoms via reaction with VOCs can then be determined using Eq. 1-3, and NIST kinetic data (Manion et al., 2014)

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

$$-d[alkenes]/dt = [X] \sum_i k_{Cl[alkene]}[alkene,i]$$  
(Eq 2)

$$-d[alkynes]/dt = [X] \sum_i k_{Cl[alkyne]}[alkyne,i]$$  
(Eq 3)

We were able to show that the simple state approach agreed well with the MCM, despite a much more simplistic approach. We used an identical approach in this work utilizing the tailpipe VOC concentrations (AQIRP, 1995). However, we further simplify the approach by using one term CH$_4$ equivalent which accounts for relative concentration and reactivity towards Cl, i.e. if a VOC reacts 1000 times faster it is the equivalent of 1000 CH$_4$ or more formally for each VOC its CH$_4$ equivalent is $k_{Cl[VOC]}/k_{Cl[CH4]}$. Whilst the approach is a simplification of course, it has been shown that using these emissions it is possible to estimate the Cl atom production in a Megacity environment and produces results that are comparable with the much more thorough modelling approach of the MCM. It also generates a metric, CH$_4$ equivalent, which can be used as a comparative measurement from city to city.

Photolysis rates were measured by a spectradiometer for O$_3$, NO$_2$, HCHO, HONO and H$_2$O$_2$. The photolysis rate of any given species was calculated by normalizing to the cross section and quantum yields taken from the recommendations of the Jet Propulsion Laboratory (JPL) kinetic evaluation report (Burkholder et al., 2015)."
“Consistent with past measurements and the measurements of this study, ClNO₂ is expected to provide a significant source of Cl during day time hours, presenting a potentially significant source of the reactive Cl atom during the day. Its rapid photolysis rate and elevated mixing ratios enables Cl to compete with OH oxidation chemistry, the known dominant daytime radical source. Here, a simple steady state calculation will be used to determine the Cl atom mixing ratio as detailed;

\[
\text{Cl}_2 + \text{hv} \rightarrow \text{Cl} + \text{Cl} \quad (1)
\]

\[
\text{ClNO}_2 + \text{hv} \rightarrow \text{Cl} + \text{NO}_2 \quad (2)
\]

\[
\text{ClONO}_2 + \text{hv} \rightarrow \text{ClO} + \text{NO}_2 \quad (3)
\]

\[
\text{HOCl} + \text{hv} \rightarrow \text{OH} + \text{Cl} \quad (4)
\]

\[
\text{OCIO} + \text{hv} \rightarrow \text{O} + \text{ClO} \quad (5)
\]

\[
\text{OH} + \text{HCl} \rightarrow \text{Cl} + \text{H}_2\text{O} \quad (6)
\]

\[
\text{Cl} + \text{O}_3 \rightarrow \text{ClO} + \text{O}_2 \quad (7)
\]

\[
\text{Cl} + \text{CH}_4 \text{ equivalent} \rightarrow \text{HCl} + \text{products} \quad (8)
\]

\[
[\text{Cl}]_{SS} = \{2J_1[\text{Cl}_2] + J_2[\text{ClNO}_2] + J_3[\text{ClONO}_2] + J_4[\text{HOCl}] + J_5[\text{OCIO}] + k_7[\text{OH}][\text{HCl}]) / (k_7[\text{O}_3] + k_8[\text{CH}_4] \text{ equivalent}) \quad (9)
\]

Where [\text{CH}_4] \text{ equivalent} represents the reactive VOC present as if it were equivalent CH4.

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

\[
[\text{Cl}]_{SS} = \{2J_1[\text{Cl}_2] + J_2[\text{ClNO}_2] + J_3[\text{ClONO}_2] + J_4[\text{HOCl}] + J_5[\text{OCIO}] + k_7[\text{OH}][\text{HCl}]) / (k_7[\text{O}_3] + k_8[\text{CH}_4] \text{ equivalent}) \quad (9)
\]

and a mean steady state OH calculated concentration of \(7 \times 10^6\) molecules cm\(^3\). Again, this approach is an estimation, but was shown to produce comparable to results with that of the more rigorous MCM approach. The main findings of this work, is that as we infer much higher concentrations of Cl atoms, as a result of much higher observed inorganic chlorine species, the impact of Cl atom chemistry is much higher than has been observed in previous work.
Figure S1. Wind rose during the campaign in Changping

Figure S2. Time series of measured ClNO₂ concentrations, modelled COₓ concentrations, and modelled CObb at the Changping site. CObb is shown for both the model using the FINN database and the GFAS database. Periods with missing measurement data are shown in grey.
Figure S3. Scatter plots of night-time averages of ClNO₂ against corresponding averages of COᵣ, COᵣᵢ in the FINN model, and COᵣᵢ in the GFAS model. Linear regressions for each of the comparisons gave the following r² results: COᵣ 0.48, COᵣᵢ FINN 0.04, and COᵣᵢ GFAS 0.21.

Figure S4. Correlation plots of measured ClNO₂ vs modelled COᵣ (green), fine seasalt (red) and course seasalt (blue).