Supplement of

Chlorine oxidation of VOCs at a semi-rural site in Beijing: significant chlorine liberation from ClNO₂ and subsequent gas- and particle-phase Cl–VOC production

Michael Le Breton et al.

Correspondence to: Michael Le Breton (michael.le.breton@gu.se)

The copyright of individual parts of the supplement might differ from the CC BY 4.0 License.
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).

\[-d[\text{alkanes}] / dt = [X \sum_i k_{\text{X-alkane}[\text{alkane},i}] \]

(Eq 1)

\[-d[\text{alkenes}] / dt = [X \sum_i k_{\text{X-alkene}[\text{alkene},i}] \]

(Eq 2)

\[-d[\text{alkynes}] / dt = [X \sum_i k_{\text{X-alkyne}[\text{alkyne},i}] \]

(Eq 3)

We were able to show that the simple state approach agreed well with a fully integrated chemical model using 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 \(k(\text{Cl} + \text{VOC}) \div k(\text{Cl} + \text{CH}_4)\). 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, albeit it with some significant error due to significant number of estimations made in a Megacity environment and produces results that are comparable with the much more thorough explicit 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;

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

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

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

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

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

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

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

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

\[
[\text{Cl}]_{\text{SS}} = \frac{2\text{J}_1[\text{Cl}_2] + \text{J}_2[\text{ClNO}_2] + \text{J}_3[\text{ClONO}_2] + \text{J}_4[\text{HOCl}] + \text{J}_5[\text{OClO}] + \text{J}_7[\text{OH}][\text{HCl}]}{\text{J}_8[\text{CH}_4]} / \text{[K}_7[\text{O}_3] + \text{K}_8[\text{CH}_4] \text{ equivalent}} \quad (9)
\]

Where [CH₄] 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) and a mean steady state OH calculated concentration of 7 x 10⁶ molecules cm⁻³. Again, this approach is an estimation but was shown to produce comparable results with that of the more rigorous explicit model using the MCM. 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.

There is a large uncertainty in the radical concentrations estimated in this work using the steady state method and this is fully acknowledged. The production rates for Cl are calculated directly from
measurements of species, e.g. ClNO₂ concentrations and their photolysis rates, estimated by a photochemical model and so that aspect of the calculation has a relatively small uncertainty. There will be missing sources of Cl production that are not measured but the main known precursors are represented in these calculations. However, the loss rate carries the bulk of the uncertainty in these calculations; first it is known that not all VOCs are measured and even after estimation of missing VOCs there will be some missing loss. Second, calibration of some VOCs in this campaign will be uncertain, hence the reporting of counts per second rather than absolute numbers. Third, the rate coefficients associated with the loss processes will carry some uncertainty too. Finally, the distribution of missing VOCs is based on USA and European emission profiles and these maybe different from those from Asia. Therefore, the uncertainty in radical concentration using this method will be at least 50%, where 20% is from rate coefficient uncertainty, taking into consideration temperature dependences, and an estimated 30% from uncertainty in concentration measurements. However, OH reactivity measurements (e.g. Yang et al., 2016) provide a direct measurement of total loss rates and although not a direct comparison with Cl loss rates they can serve as a guide. Using 20s⁻¹ as an estimate for the total loss rate for OH the steady state calculations are predicting loss rates in the range 10-15 s⁻¹. Therefore, a 50% uncertainty and recognising that the concentrations generated are almost certainly an upper limit provides some further context to these calculations.

Figure S1. Wind rose during the campaign in Changping
Figure S2. Time series of measured ClNO$_2$ concentrations, modelled CO$_t$ concentrations, and modelled CO$_{bb}$ at the Changping site. CO$_{bb}$ 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 ClNO$_2$ against corresponding averages of CO$_t$, CO$_{bb}$ in the FINN model, and CO$_{bb}$ in the GFAS model. Linear regressions for each of the comparisons gave the following r$^2$ results: CO$_t$ 0.48, CO$_{bb}$ FINN 0.04, and CO$_{bb}$ GFAS 0.21.
Figure S4. Correlation plots of measured ClNO₂ vs modelled COt (green), fine seasalt (red) and course seasalt (blue).