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Supplementary material

Chlorine chemistry in urban atmospheres: a review

C. B. Faxon[A,B] *and D. T. Allen*[A]

[A]Center for Energy and Environmental Resources, University of Texas, M/C 27100, 10100 Burnet Road, Austin, TX 78758

[B]Corresponding author. Email: cfax@utexas.edu

Sensitivity of predicted ozone and $ClNO_2$ concentrations to rate parameter estimates for the heterogeneous $ClNO_2$ production mechanism

Simulation methods

The SAPRC software developed by Dr William Carter at UC Riverside was used in the box modelling for the parameter analysis. The CB05 condensed photochemical mechanism[1] was modified to include the parameterisations of the heterogeneous mechanism. Simulations were run from sunset to sunset for a 24-h period. Initial conditions included ozone and NO_x concentrations of 50 and 20 ppbv. The heterogeneous mechanism was modelled as a pseudo first order reactions by the expressions shown below.

$$-\frac{\mathrm{d}[\mathrm{N_2O_5}]}{\mathrm{d}t} = \frac{1}{4}\gamma\omega A[\mathrm{N_2O_5}] \quad \text{(S1)}$$

$$\frac{\mathrm{d}[\mathrm{ClNO_2}]}{\mathrm{d}t} = \frac{1}{4}\gamma\omega Y_{\mathrm{ClNO_2}} A[\mathrm{N_2O_5}] \quad \text{(S2)}$$

VOC surrogate mixture

The mixture of VOCs was a surrogate mixture formulated to represent an average urban VOC mixture. The formulation was based on EPA data collected from 1985 to1988 in 66 US cities and has been used extensively since in both measurement and modelling studies. The 182 species represented in this dataset were condensed to the nine representative reactive species present in the surrogate mixture. The condensed mixture represents the same overall reactivity, per parts per million by volume of carbon (ppm C), as the original mixture. An 'inert or lost carbon' category is included to represent the compounds that were removed because of low reactivities or condensed into smaller representative species. Table S1 shows the constituents of the mixture.[2]

Table S1. Surrogate VOC mixture composition

Species	CB05 Species	ppb ppm^{-1} C
n-Butane	4 PAR	70.7
n-Octane	7 PAR, 1 NR	22.3
Ethylene	ETH	13.4
Propene	1 PAR, 1 OLE	10.4
t-2-Butene	IOLE	10.4
Toluene	TOL	13.3
m-Xylene	XYL	16.3
Formaldehyde	FORM	7.9
Acetaldehyde	ALD2	7.6
Inert or lost carbon	NR	193.1

Parameter value ranges

The reactive uptake was varied between 0 and 0.038, an upper limit determined from the literature[3–6] Particle surface area was approximated by assuming a trimodal particle distribution, with 30, 50 and 20 % (by mass) having average diameters of 0.1, 0.5 and 1.0 μm. In the simulations presented here, an aerosol concentration of 15 μg m^{-3} was used. $ClNO_2$ yield was varied between zero and one to correspond with the wide range of yield values reported in the literature.[3,5–9] VOC levels were varied between 0 and 1000 ppb C with a value of 300 ppb C considered to be a level representing a moderate urban concentration of VOCs.

Results and discussion

The heterogeneous N_2O_5–$ClNO_2$ mechanism is able to reproduce $ClNO_2$ concentrations that have been observed in the environment within parameter ranges used in this study. Depending on the combination of heterogeneous parameters, VOCs and NO_x, the mechanism contributed to both peak ozone reduction as well as peak ozone increases. The range was a –10.5 to 27 % change in peak O_3 concentrations relative to the base case scenario containing no heterogeneous chemistry. The decreases in ozone typically resulted from low values of $ClNO_2$ yield (0–15 %) depending on the amount and types of VOCs present). This was likely due to a higher conversion rate of NO_x into nitric acid at lower $ClNO_2$ yield values, which simultaneously reduced the amount of $ClNO_2$ produced. Combinations of yields above 25 % and reactive uptake coefficients greater than zero resulted in increases in peak ozone levels.

The effect of changing base VOC concentrations was also examined. Four scenarios with differing initial VOC concentrations were used: (1) 0 ppb C VOCs; (2) 300 ppb C VOCs; (3) 1000 ppb C VOCs; (4) 300 ppb C *t*-2-butene. The reason for isolating the effects of *t*-2-butene within a single scenario is that it rapidly reacts with $NO_3^{\bullet}$, thus producing HNO_3 instead of N_2O_5 through the reaction of $NO_3^{\bullet}$ with NO_2. For all values of γ examined, the effect of increasing the value of the yield parameter from 0 to 100 % at a fixed γ was a linear increase in peak ozone concentrations. This is summarised in Fig. S1.

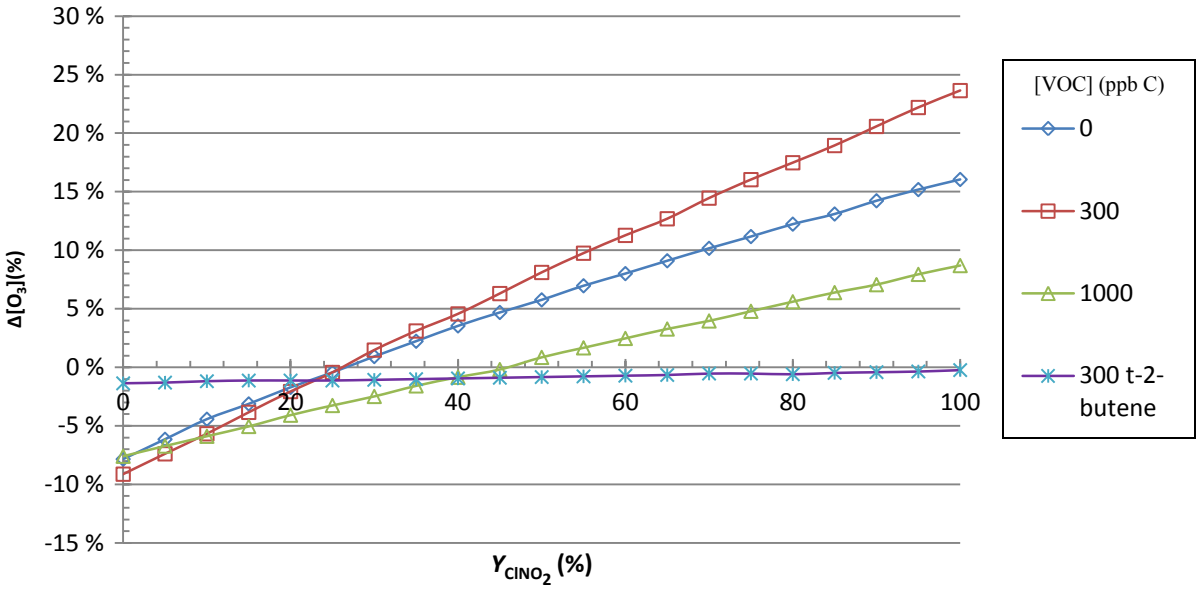

Fig. S1. Differences in peak O_3 concentrations (%) compared to base case scenarios where the base case scenario assumes no heterogeneous reaction of N_2O_5. Surface area equivalent to PM = 15 μg m^{-3} as described in the Methods section.

Fig. S2 shows the corresponding peak $ClNO_2$ concentrations during the yield variation scenarios.

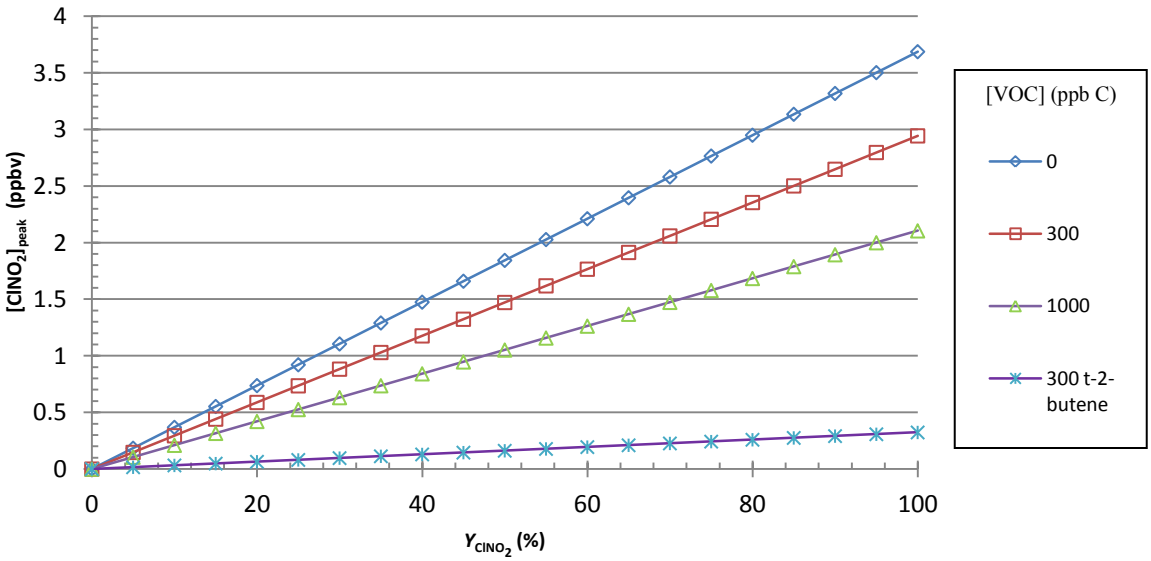

Fig. S2. Peak $ClNO_2$ concentrations from box modelling simulations.

For variations in the reactive uptake coefficient, $ClNO_2$ yield values were held constant at values ranging between 0 and 100 % while the reactive uptake was varied between its lower and upper limits in sequential simulations. The effect of increases in the reactive uptake at a fixed yield value was an intensification of the effect on peak ozone concentrations elicited by the yield value. Fig. S3 summarises

the effects of these variations on peak ozone formation in simulations where surface area was set to correspond to a particle concentration of 15 μg m^{-3} and the VOC concentration was 300 ppb C. Fig. S4 shows the peak $ClNO_2$ production from the same set of simulations.

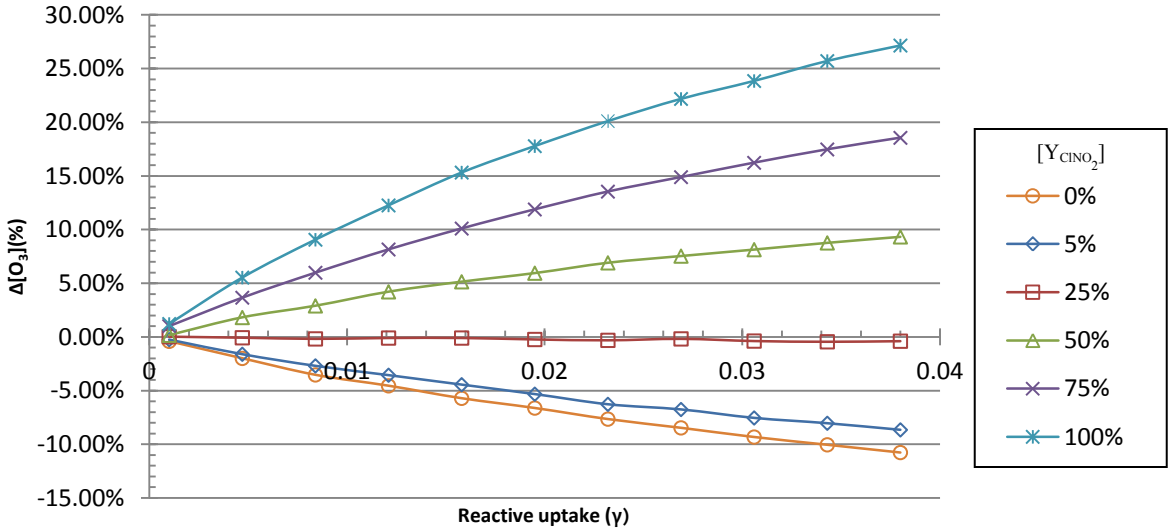

Fig. S3. Resulting peak O_3 increases over base case scenario (no heterogeneous reaction) from reactive uptake variation.

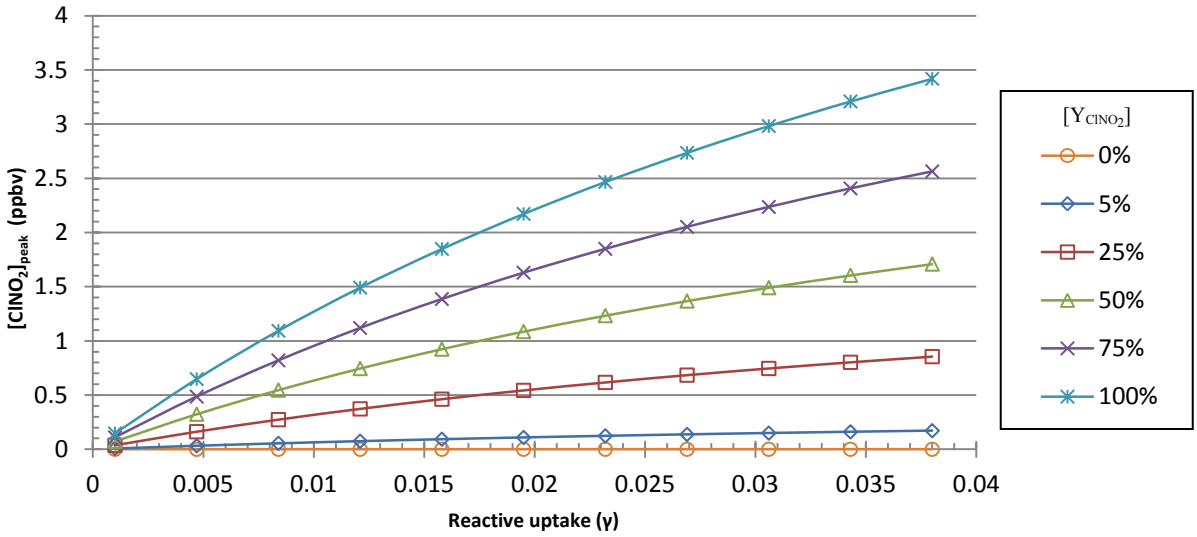

Fig. S4. Resulting peak $ClNO_2$ concentrations from reactive uptake variation.

Effects of multi-parameter variation

The combined effects of the variation of multiple parameters can also be examined. As the contour plots in Figs S5 and S6 below show, higher combinations of parameter values lead to higher peak

concentrations of $ClNO_2$ in the morning as well as larger increases in peak O_3 concentrations over the base case simulation in which no heterogeneous chlorine chemistry was included. However, the variation of different parameters results in different effects. For example, a 10.8 ppbv increase in peak ozone over the base case peak concentration (74.8 ppb) results from initial conditions of 300 ppb C of VOC surrogate, a reactive uptake coefficient of 0.03 and a yield value of 0.75. By fixing reactive uptake at a value of 0.03 and increase yield from 0 to 0.75, the resulting increase in peak ozone concentration is 18.82 ppbv. However, fixing the yield parameter at a value of 0.75 and increasing the reactive uptake from 0 to 0.03 results in maximum ozone increase of 12.14 ppbv. These results illustrate the range of ozone effects that can be achieved using rate parameters within accepted ranges. In the results discussed here, a particle surface area equivalent to a population of 15 μg m^{-3} was used.

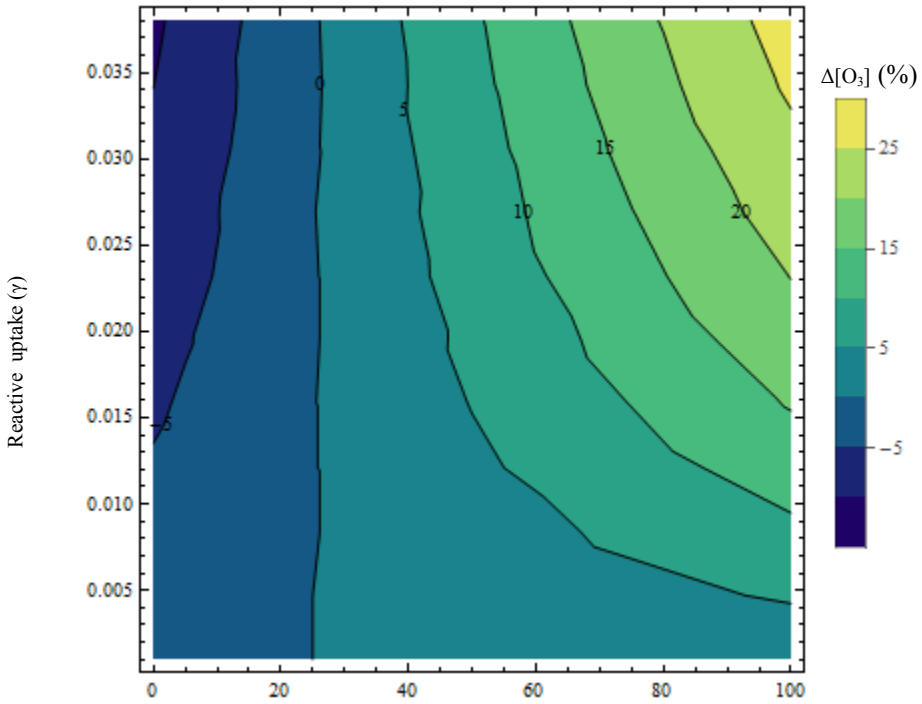

Fig. S5. Percentage peak O_3 increases in over the base case scenario (no heterogeneous reactions) for various combinations of the $ClNO_2$ yield and reactive uptake parameter values.

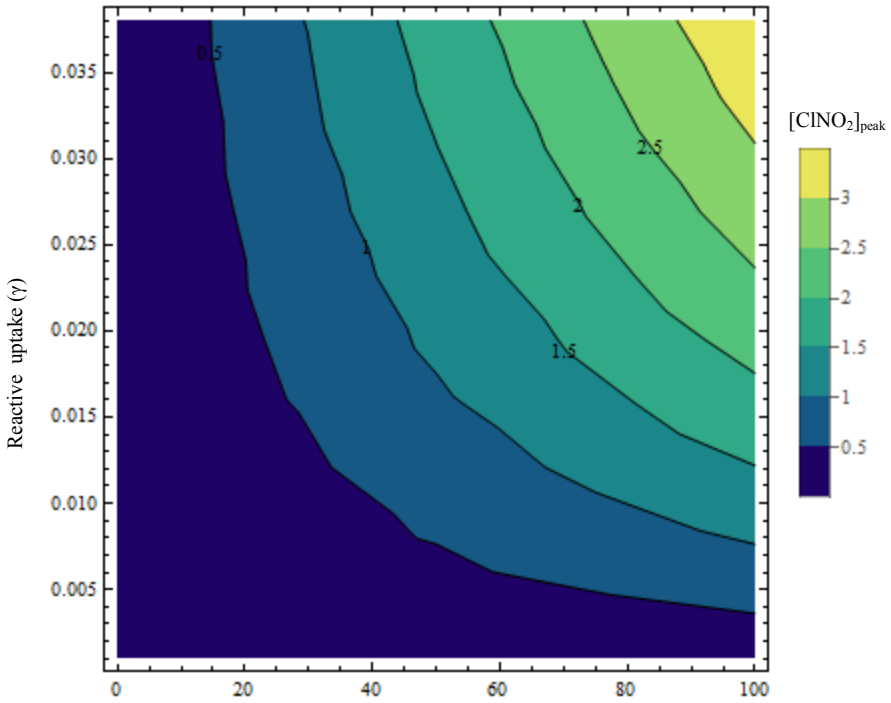

Fig. S6. Peak $ClNO_2$ concentrations (ppb) for various combinations of the $ClNO_2$ yield and reactive uptake parameter values.

References

[1] G. Yarwood, S. Rao, M. Yocke, G. Z. Whitten, *Updates to the carbon bond chemical mechanism: CB05, Final report prepared for US EPA RT-04-00675* **2005** (Environ: Novato, CA).

[2] W. P. L. Carter, D. Luo, I. L. Malkina, J. A. Pierce, *Environmental chamber studies of atmospheric reactivities of volatile organic compounds. Effects of varying ROG surrogate and NO_x, final report to California Air Resources Board, Contract A032-096* **1995** (California Air Resources Board: Sacramento, CA). Available at http://www.cert.ucr.edu/~carter/pubs/explrept.pdf [Verified 7 May 2013].

[3] J. A. Thornton, J. P. Kercher, T. P. Riedel, N. L. Wagner, J. Cozic, J. S. Holloway, W. P. Dubé, G. M. Wolfe, P. K. Quinn, A. M. Middlebrook, B. Alexander, S. S. Brown, A large atomic chlorine source inferred from mid-continental reactive nitrogen chemistry. *Nature* **2010**, *464*, 271. doi:10.1038/NATURE08905

[4] F. Schweitzer, P. Mirabel, C. George, Multiphase chemistry of N_2O_5, $ClNO_2$, and $BrNO_2$. *J. Phys. Chem. A* **1998**, *102*, 3942. doi:10.1021/JP980748S

[5] W. Behnke, H.-U. Krüger, V. Scheer, C. Zetzsch, Formation of Atomic Cl from sea spray via photolysis of nitryl chloride: determination of the sticking coefficient of N_2O_5 on NaCl aerosol. *J. Aerosol Sci*. **1991**, *22*, S609. doi:10.1016/S0021-8502(05)80175-2

[6] J. M. Roberts, H. D. Osthoff, S. S. Brown, A. R. Ravishankara, D. Coffman, P. Quinn, T. Bates, Laboratory studies of products of N2O5 uptake on Cl-containing substrates. *Geophys. Res. Lett*. **2009**, *36*, L20808. doi:10.1029/2009GL040448

[7] W. Behnke, C. George, V. Scheer, C. Zetzsch, Production and decay of $ClNO_2$ from the reaction of gaseous N_2O_5 with NaCl solution: bulk and aerosol experiments. *J. Geophys. Res.* **1997**, *102*, 3795. doi:10.1029/96JD03057

[8] J. M. Roberts, H. D. Osthoff, S. S. Brown, A. R. Ravishankara, N_2O_5 oxidizes chloride to Cl_2 in acidic atmospheric aerosol. *Science* **2008**, *321*, 1059. doi:10.1126/SCIENCE.1158777

[9] J. A. Thornton, J. P. D. Abbatt, N_2O_5 reaction on submicron sea salt aerosol: kinetics, products, and the effect of surface active organics. *J. Phys. Chem. A* **2005**, *109*, 10004. doi:10.1021/JP054183T