Supplementary Material

Inland Concentrations of Cl₂ and ClNO₂ in Southeast Texas Suggest Chlorine Chemistry Significantly Contributes to Atmospheric Reactivity. *Atmosphere* 2015, *6*, 1487-1506, doi:10.3390/atmos6101487

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S1. Calibration of the HR-ToF-CIMS

Calibrations were performed for each species and indicated a linear response across the concentrations observed during the campaign. Calibration curves were generated as linear least squares fits to the correlation between known measured concentrations and normalized analyte signals. Analyte signals were normalized by the sum of I^- and IH_2O^- ion signals. Instrument response to Cl_2 was calibrated directly from sequential dilutions of standards of known concentration (Airgas). The resulting Cl_2 calibration curve is shown in Figure S1.

Calibration of the $ClNO_2$ signal response was performed by passing a known concentration of Cl_2 over wet $NaNO_2$ salt to generate $ClNO_2$ by the reaction $Cl_2 + NaNO_2 \rightarrow NaCl + ClNO_2$, as cited by previous work [1–5]. The wet salt bed was placed in the inlet (2.5" length × 0.25" inner diameter) of a glass bulb, and the residence time for reaction of Cl_2 was calculated to be approximately 0.24 s. The exact technique for this calibration in previous work has varied with some authors using $NaNO_2$ salt [1,4] and others using a combination of $NaCl$ and $NaNO_2$ [3,5]. Thaler *et al.* (2011) suggest that "a marginal increase in $ClNO_2$ yield" is obtained from the addition of $NaCl$. Furthermore, one study, [1] citing previous work [6,7], estimates a ±25% uncertainty in the measured sensitivity of $ClNO_2$ using this calibration method, which appears much larger than differences in the yield using pure $NaNO_2$ and a mixture of $NaNO_2$ and $NaCl$. We therefore estimate the yield of $ClNO_2$ from the heterogeneous reaction of Cl_2 with $NaNO_2$ salt is 100% with an uncertainty of 25%. Similarly, N_2O_5 was calibrated for by passing N_2O_5 over a wetted $NaCl$ bed to produce $ClNO_2$. The decrease in N_2O_5 from the reaction with

NaCl was assumed to be equal to the concentration of $ClNO_2$ produced (*i.e.*, a 100% yield) [8,9]. The calibration curves for $ClNO_2$ and N_2O_5 are shown in Figures S2 and S3, respectively.
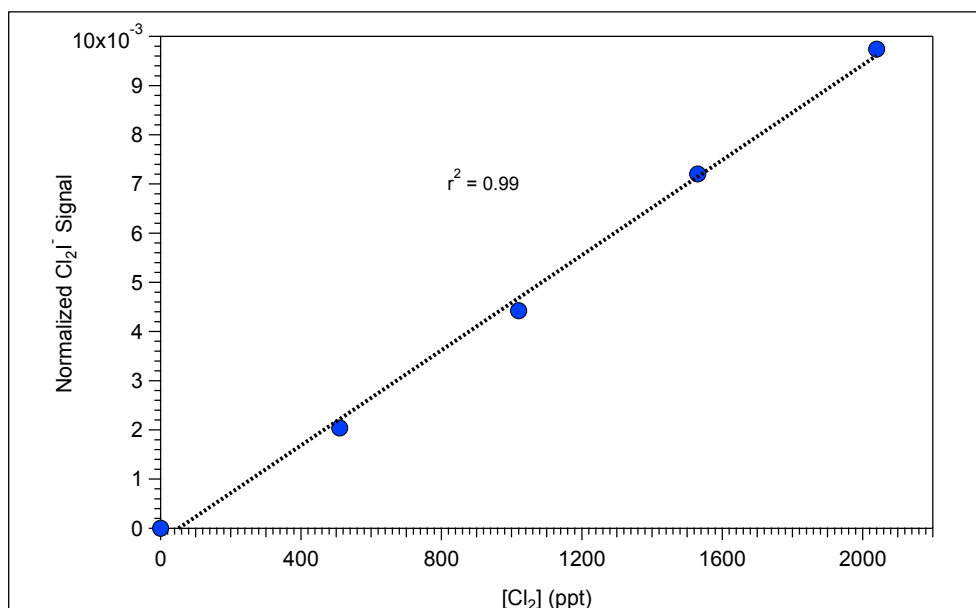

Figure S1. Calibration Curve for Cl_2 as quantified by normalized Cl_2I^- signal in the HR-ToF-CIMS. Reagent ion signal during the calibration was approximately 2.1×10^6 ions·s^{-1}.
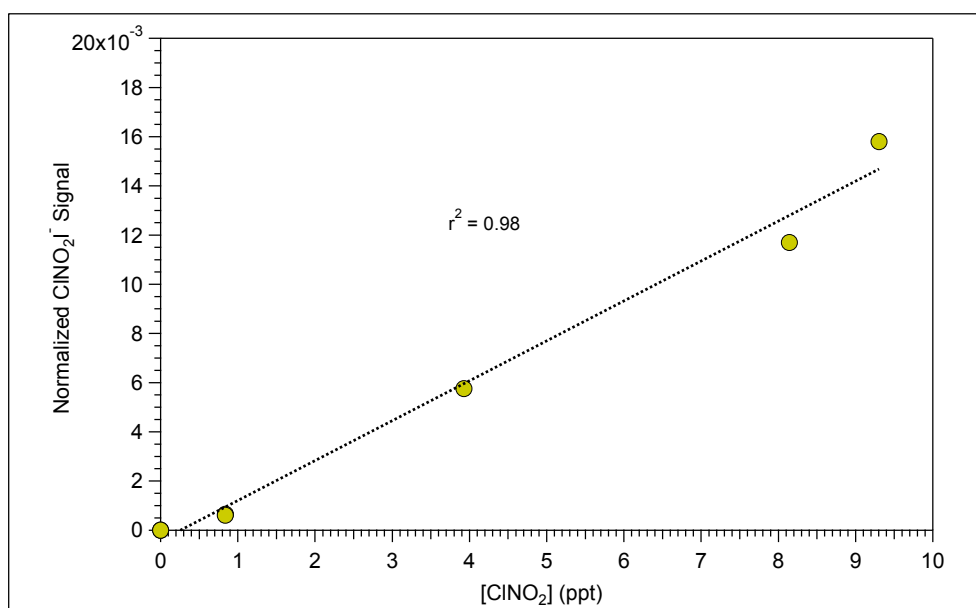

Figure S2. Calibration Curve for $ClNO_2$ as quantified by normalized $ClNO_2I^-$ signal in the HR-ToF-CIMS. The reagent signal during calibration was approximately 1.6×10^6 ions·s^{-1}.
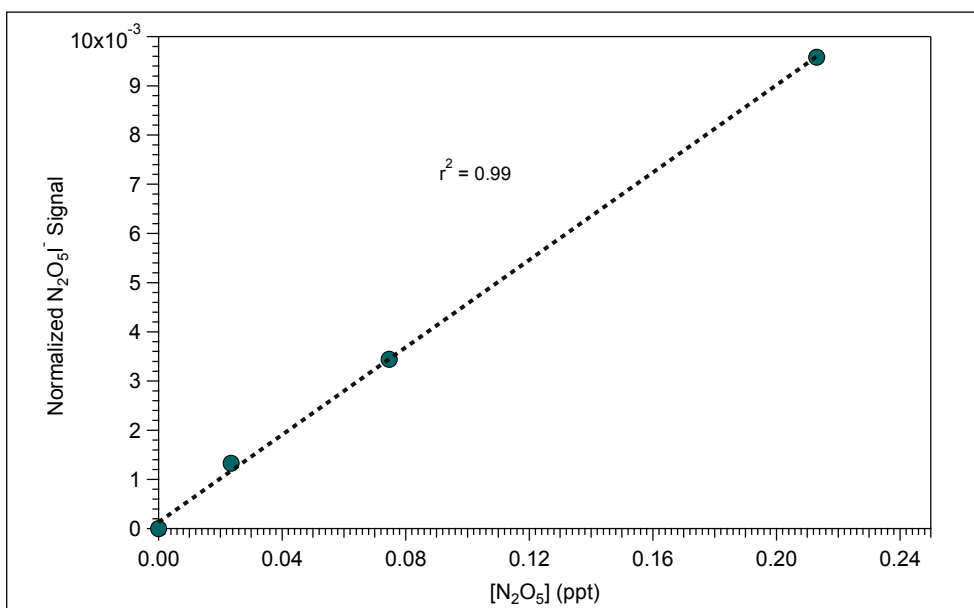
Figure S3. Calibration Curve for N₂O₅ as quantified by normalized N₂O₅I⁻ signal in the HR-ToF-CIMS. Reagent ion signal during the calibration was approximately 2×10^6 ions·s⁻¹.

Detection limits were determined for each species using the formula shown in Equation (S1) [7].

$$S/N = C_f[X]t/\sqrt{C_f[X]t + 2Bt}$$ (S1)

In this equation, C_f(Hz·ppt⁻¹) is the calibration coefficient for the species and B (Hz) is the underlying background count rate. *S/N* is the signal to noise ratio, which was set to 2 to be consistent with the statistical definition of a detection limit. The detection limit of the measured species, [*X*], is determined for an integration period, *t* (s). For Cl₂, ClNO₂ and N₂O₅, the calculated detection limits were 0.4, 1.4 and 0.3 pptᵥ over a sampling period of 2 s.

S2. Modified Version of the Carbon Bond 6 Photochemical Mechanism

The Carbon Bond 6 mechanism was modified to include basic gas phase chlorine reactions, as well as ClNO₂ photolysis. The full list of reactions that were added is shown in Table S1.
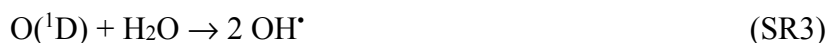
Table S1. List of chlorine reactions added to the Carbon Bond 6 (CB6r2) mechanism for the simulations discussed in this work. Species are written in terms of their CB6r2 identities.

Reaction #	Reactants	Products
1	CL2 + *hv*	2 CL
2	HOCl + *hv*	OH + CL
3	CL + O3	CLO
4	CLO + CLO	0.3 C2 + 1.4 CL
5	CLO + NO	CL + NO2
6	CLO + HO2	HOCL
7	CLO + NO2	N3CL
8	N3CL + *hv*	CLO + NO2
9	N3CL + *hv*	CL + NO3
10	CL + N3CL	CL2 + NO3
11	OH + HCL	CL
12	OH + FMCL	CL + CO
13	FMCL + *hv*	CL + CO + HO2
14	CL + H2	HCL + HO2
15	CL + CH4	HCL + MEO2
16	CL + PAR	HCL + 0.87 XO2 + 0.13 XO2N + 0.11 HO2 + 0.06 ALD2 − 0.11 PAR + 0.76 ROR + 0.05 ALDX
17	CL + ETHA	HCL + 0.991 ALD2 + 0.991 XO2 + 0.009 XO2N + HO2
18	CL + ETH	FMCL + 2 XO2 + HO2 + FORM
19	CL + OLE	0.13 HCL + 0.87 FMCL + 0.58 ALD2 + 0.29 ALDX + 0.13 OLE + 0.13 FORM + 1.87 XO2 + HO2 - PAR
20	CL + IOLE	0.2 HCL + 0.8 FMCL + 0.27 ALD2 + 0.53 ALDX + 0.2 OLE + 0.2 FORM + 0.2 PAR + 1.8 XO2 + HO2
21	CL + ISOP	0.15 HCL + 0.85 FMCL + 0.92 ISPD + 1.7 XO2 + 0.08 XO2N + 0.92 HO2
22	CL + TERP	0.4 HCL + 0.6 FMCL + 0.45 ALDX + 1.8 PAR + 1.2 XO2 + 0.25 XO2N + 0.75 HO2
23	CL + TOL	HCL + 0.88 XO2 + 0.12 XO2N + 0.84 +HO2
24	CL + XYL	HCL + 0.84 XO2 + 0.16 XO2N + 0.84 HO2
25	CL + FORM	HCL + HO2 + CO
26	CL + ALD2	HCL + C2O3
27	CL + ALDX	HCL + CXO3
28	CL + MEOH	HCL + HO2 + FORM
29	CL + ETOH	HCL + HO2 + ALD2
30	ClNO2 + *hv*	CL + NO2

S3. Derivation of the OH˙ Production Rate Used in Box Modeling Simulations

Equation 1 in the main text was used to calculate the rate of OH˙ production, and was derived from the rate equation for the reaction of primary reactions of the radical species, $O(^1D)$ (Reaction (SR1)), with H_2O, N_2 and O_2 (Reactions (SR2) and (SR3)). The rate of $O(^1D)$ formation was calculated from the simulated rate of O_3 photolysis. These three primary reactions of $O(^1D)$ were combined in a rate expression to determine the concentration of $O(^1D)$. Using Reaction (SR2) as the primary source of OH˙

production, Equations (S2) and (S3) were combined to calculate the rate of OH$^\bullet$ production as shown in Equation (S4).

$$O_3 + h\nu \rightarrow O(^1D) + O_2 \quad\quad\quad \text{(SR2)}$$

$$O(^1D) + H_2O \rightarrow 2\ OH^\bullet \quad\quad\quad \text{(SR3)}$$

$$O(^1D) + M \rightarrow O + M \quad\quad\quad \text{(SR4)}$$

$$0 = d[(O^1D)]/dt = J_{S1}[O_3] - k_{S2}[O^1D][H_2O] - k_{S3}[O^1D][M] \quad\quad\quad \text{(S2)}$$

$$P_{OH} = d[OH]/dt = 2k_{S2}[(O^1D)][H_2O] \quad\quad\quad \text{(S3)}$$

$$P_{OH} = 2J_{(S1)}[O_3]k_{H_2O}[H_2O]/(k_{H2O}[H_2O] + k_{N2}[N_2] + k_{O2}[O_2]) \quad\quad\quad \text{(S4)}$$

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