SUPPORTING INFORMATION

An MCM modeling study of nitryl chloride ($ClNO_2$) impacts on oxidation, ozone production and nitrogen oxide partitioning in polluted continental outflow

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Supplemental Figures and Tables

Pasadena (GC-MS)	R/V Atlantis (GC-FID)	R/V Atlantis (PTR-ToF-MS)	median (pptv)	1σ
methanol	methanol		1220	180
ethanol			1540	200
isopropanol			320	50
ethanal	ethanal		370	150
methacrolein			10	10
propanal			90	20
butanal			20	4
ethane			3120	440
propane		propane	1940	330
i-butane		i-butane	510	70
n-butane		n-butane	1200	190
i-pentane			780	100
n-pentane		n-petane	350	40
hexane			250	30
nonane			40	2
decane			36	2
undecane			34	4
ethene		ethene	900	100
propene		propene	250	60
cis-2-butene			10	2
1-butene		1-butene	25	5
2-methylpropene			80	20
1,3-butadiene			44	17
trans-2-butene			33	7
ethyne		ethyne	320	40
propylbenzene			15	1
isopropylbenzene			5	1
benzaldehyde			40	8
benzene	benzene	benzene	65	5
ethylbenzene			25	2
o-methylethylbenzene			4	1
1,3,5-trimethylbenzene			10	3
phenylethene			14	2
1,2,4-trimethylbenzene			25	5
o-xylene			30	3
toluene	toluene	toluene	140	13
1,2,3-trimethylbenzene			8	2
methylvinylketone			16	25
acetone	acetone		740	260
methylethylketone			53	27
alphapinene			13	8
betapinene			8	4
limonene			9	7
isoprene			30	180

Table S-1. VOC measured during CalNex 2010 at the Pasadena, CA, ground site and aboard the R/V *Atlantis* and used as model constraints. Medians and standard deviations for the diurnal values used in the model are also given.

Reaction*	k**
N2O5 → CLNO2 + HNO3	$\gamma\omega S_A / 4$
	$\phi\gamma\omega S_A / 4$ (for $ClNO_2$ formation)
	$(2-\phi)\gamma\omega S_A / 4$ (for HNO_3 formation)
CLNO2 + hv → CL + NO2	j_{ClNO2}
CL + CH3OH → HCHO + HO2 + HCL	1.4e-10*exp(-280/T)
CL + C2H5OH → CH3CHO + HO2 + HCL	0.92*6.0e-11*exp(155/T)
CL + C2H5OH → HOCH2CH2O2 + HCL	0.08*6.0e-11*exp(155/T)
CL + IPROPOL → CH3COCH3 + HO2 + HCL	7.4e-11
CL + IPROPOL → IPROPOLO2 + HCL	1.3e-11
CL + C2H4 → CH2CLCH2O2	1.1e-10
CL + C3H6 → CH2CLCHOOCH3	0.4*2.7e-10
CH2CLCHOOCH3 + NO → CH2CLCOCH3	2.9e-12*exp(350/T) (k from MCM for NC3H7O2+NO)
CL + C3H6 → CH3CHCLCH2OO	0.5*2.7e-10
CH3CHCLCH2OO + NO → CHOCHCLCH3	2.9e-12*exp(350/T) (k from MCM for NC3H7O2+NO)
CHOCHCLCH3 + NO3 → C2H5CLCO3	3.24e-12*exp(-1860/T) (k from MCM for propanal+NO3)
CHOCHCLCH3 + OH → C2H5CLCO3	4.9e-12*exp(405/T) (k from MCM for propanal+OH)
C2H5CLCO3 + HO2 → CH3CHCLO2	KAPHO2*0.44 (k from MCM for C2H5CO3+HO2)
C2H5CLCO3 + HO2 → CH3CHCLCO3H	KAPHO2*0.41 (k from MCM for C2H5CO3+HO2)
CH3CHCLCO3H + OH → C2H5CLCO3	4.42e-12 (k from MCM for PERPROACID+OH)
CH3CHCLCO3H + hv → CH3CHCLO2 + OH	j-value for PERPROACID from MCM
C2H5CLCO3 + HO2 → CH3CHCLCOOH + O3	KAPHO2*0.15 (k from MCM for C2H5CO3+HO2)
CH3CHCLCOOH + OH → CH3CHCLO2	1.2e-12 (k from MCM for PROPACID+OH)
C2H5CLCO3 + NO → CH3CHCLO2 + NO2	6.7e-12*exp(340/T) (k from MCM for C2H5CO3+NO)
C2H5CLCO3 + NO2 → 2CLPPN	KFPAN (k from MCM for C2H5CO3+NO2)
2CLPPN + OH → CLETAL + CO + NO2	1.27e-12 (k from MCM for PPN+OH)
2CLPPN → C2H5CLO3 + NO2	1.7e-3*exp(-11280/T) (k from MCM for PPN decomposition)
C2H5CLCO3 + NO3 → CH3CHCLO2	KRO2NO3*1.74 (k from MCM for C2H5CO3+NO3)
C2H5CLCO3 → CH3CHCLO2	1.00e-11*0.7 (k from MCM for C2H5CO3 +RO2→C2H5O2)
C2H5CLCO3 → CH3CHCLCOOH	1.00e-11*0.3 (k from MCM for C2H5CO3 +RO2→PROPACID)
CHOCHCLCH3 → CH3CHCLO2 + HO2 + CO	j-value for propanal+hv from MCM
CL + C3H6 → CH2C2H3O2 + HCL	0.1*2.7e-10 %at 298K
CH2C2H3O2 + NO → ACR	KRO2NO (k from MCM for ISOPDO2+NO)
CL + HCHO → HO2	8.1e-11*exp(-34/T)
CL + CH3CHO → CH3CO3	8e-11
CL + C2H5CHO → C2H5CO3	1.3e-10
CL + CH3COCH3 → CH3COCH2O2	1.5e-11*exp(-590/T)
CL + BENZENE → products	1.5e-15 (Shi and Bernhard, 1997)
CL + STYRENE → products	3.6e-10 (Shi and Bernhard, 1997)
CL + OXYL → products	1.5e-10 (Shi and Bernhard, 1997)
CL + TOLUENE → products	5.9e-11 (Shi and Bernhard, 1997)
OH + HCL → CL	2.6e-12*exp(-350/T)

CL + O3 → CLO	2.8e-11*exp(-250/T)
CLO + NO → CL + NO2	6.2e-12*exp(295/T)
CLO + HO2 → HOCL	2.2e-12*exp(340/T)
CLO + NO2 → CLONO2	2.3399e-12
CLONO2 + hv → CL + NO3	$j_{ClONO2 + hv \rightarrow Cl + NO3}$
CLONO2 + hv → CLO + NO2	$j_{ClONO2 + hv \rightarrow ClO + NO2}$
HOCL + hv → CL + OH	$j_{HOCl + hv \rightarrow Cl + OH}$
CLONO2 → CL2 + HNO3	$\gamma\omega S_A / 4$
HOCL → CL2	$\gamma\omega S_A / 4$
CL2 + hv → 2CL	$j_{Cl2 + hv \rightarrow 2Cl}$
C5H8 + CL → products	4.27e-10

*The MCM designated name is provided for reactants and products (i.e. NO_2 = NO2, isopropanol = IPROPOL, etc.). Newly added species are assigned names similar to the MCM naming convention (i.e. $ClNO_2$ = CLNO2).

**When available, the temperature dependent rate constants are provided. Otherwise rate constants are for 298K.

γ = uptake coefficient for the given reactant with aerosol surface area; ϕ = product yield; ω = mean molecular speed of the given reactant (m/s); S_A = aerosol surface area concentration (m^2/m^3)

References:

Shi, J., and Bernhard, M. J.: Kinetic studies of Cl-atom reactions with selected aromatic compounds using the photochemical reactor-FTIR spectroscopy technique, International Journal of Chemical Kinetics, 29, 349-358, doi: 10.1002/(SICI)1097-4601(1997)29:5<349::AID-KIN5>3.0.CO;2-U, 1997.

Table S-2. Additional non-MCM reactions and associated rate constants used by the model.

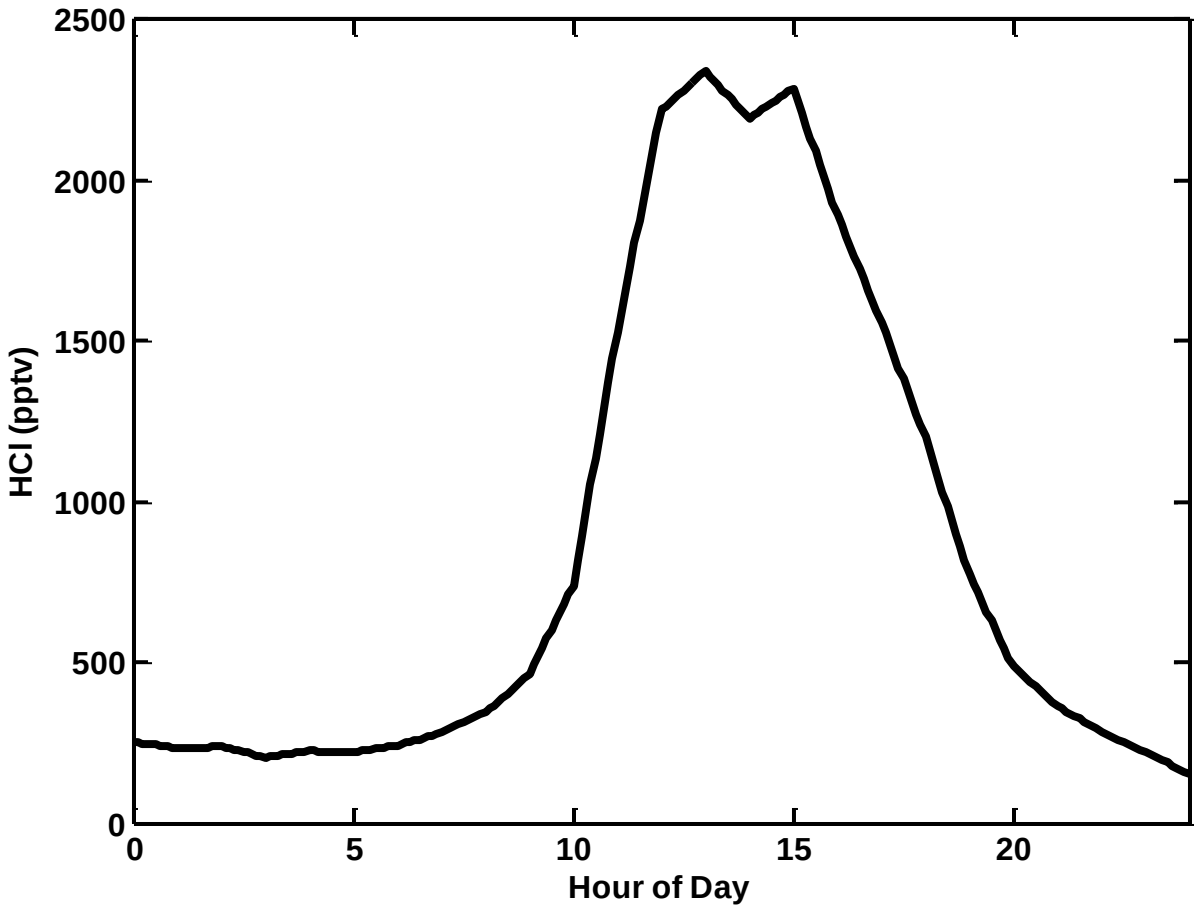

Figure S-1. Hydrochloric acid (HCl) diurnal profile used in the model.

Figure S-2. Methanol oxidation mechanism by atomic chlorine added to the model reactions.

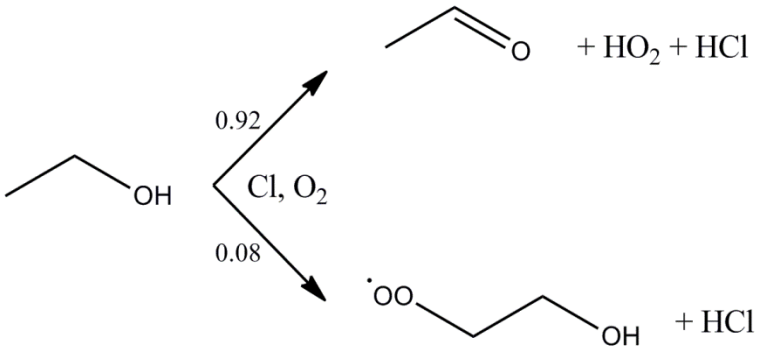

Figure S-3. Ethanol oxidation mechanism by atomic chlorine added to the model reactions.

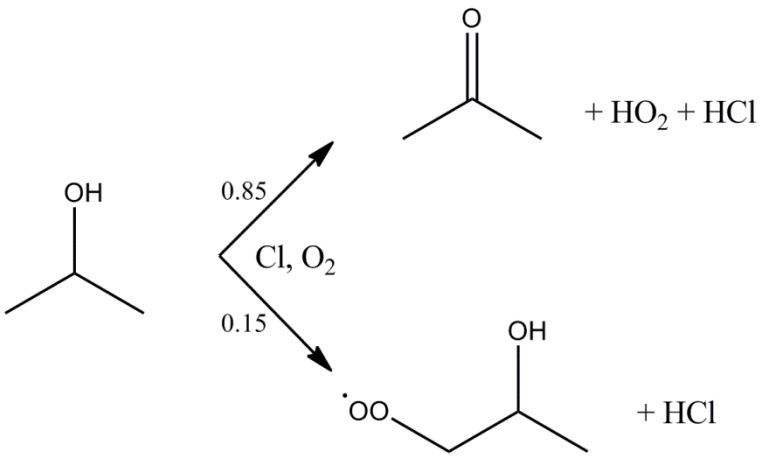

Figure S-4. Isopropanol oxidation mechanism by atomic chlorine added to the model reactions.

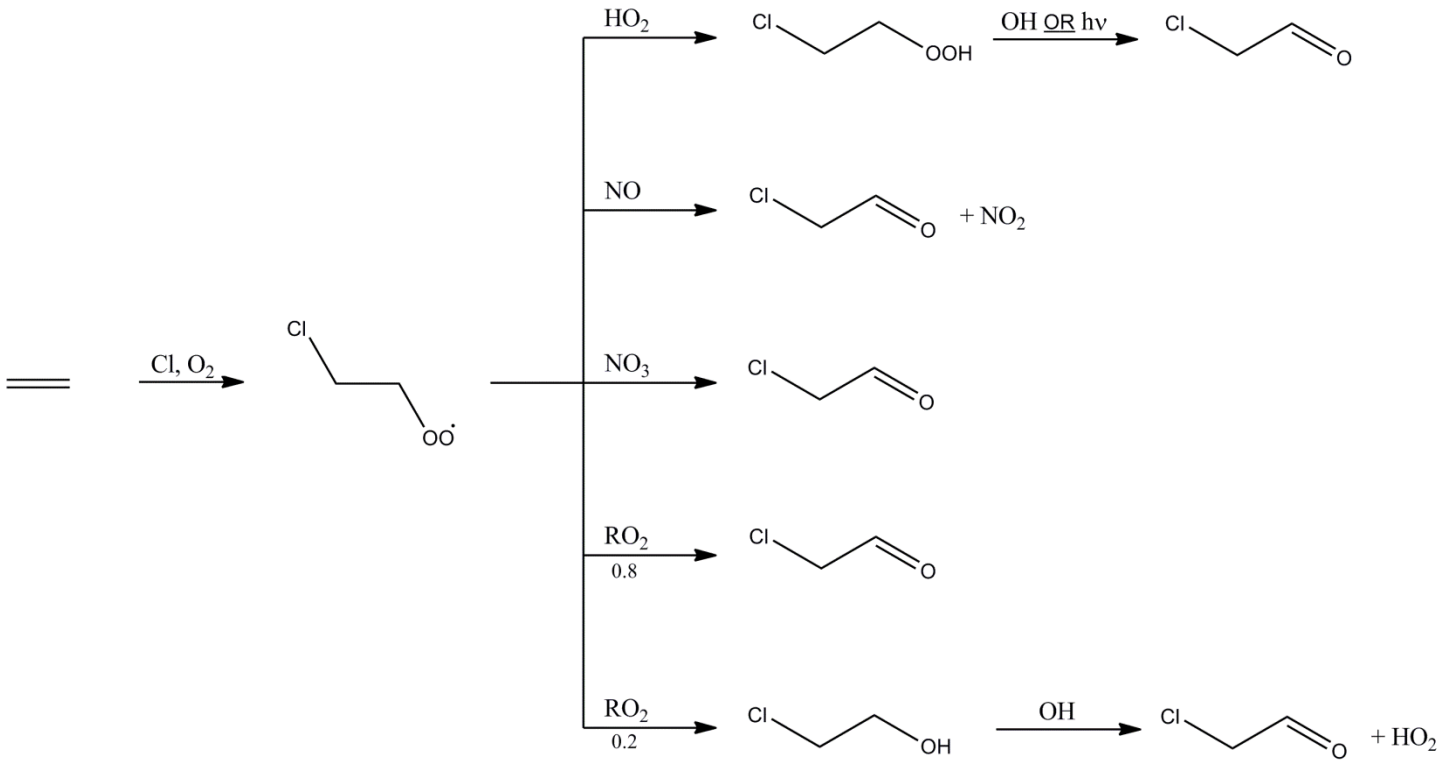

Figure S-5. Ethene oxidation mechanism by atomic chlorine added to the model reactions.

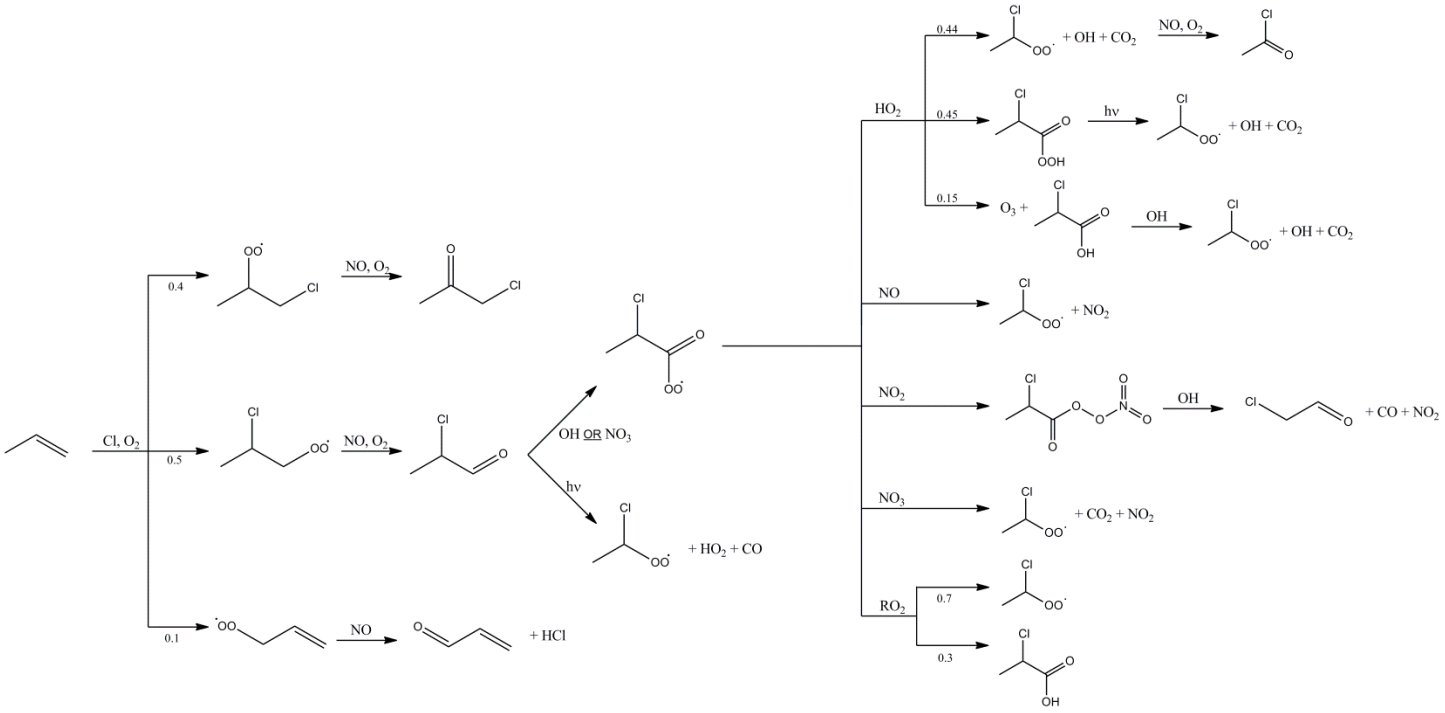

Figure S-6. Propene oxidation mechanism by atomic chlorine added to the model reactions.

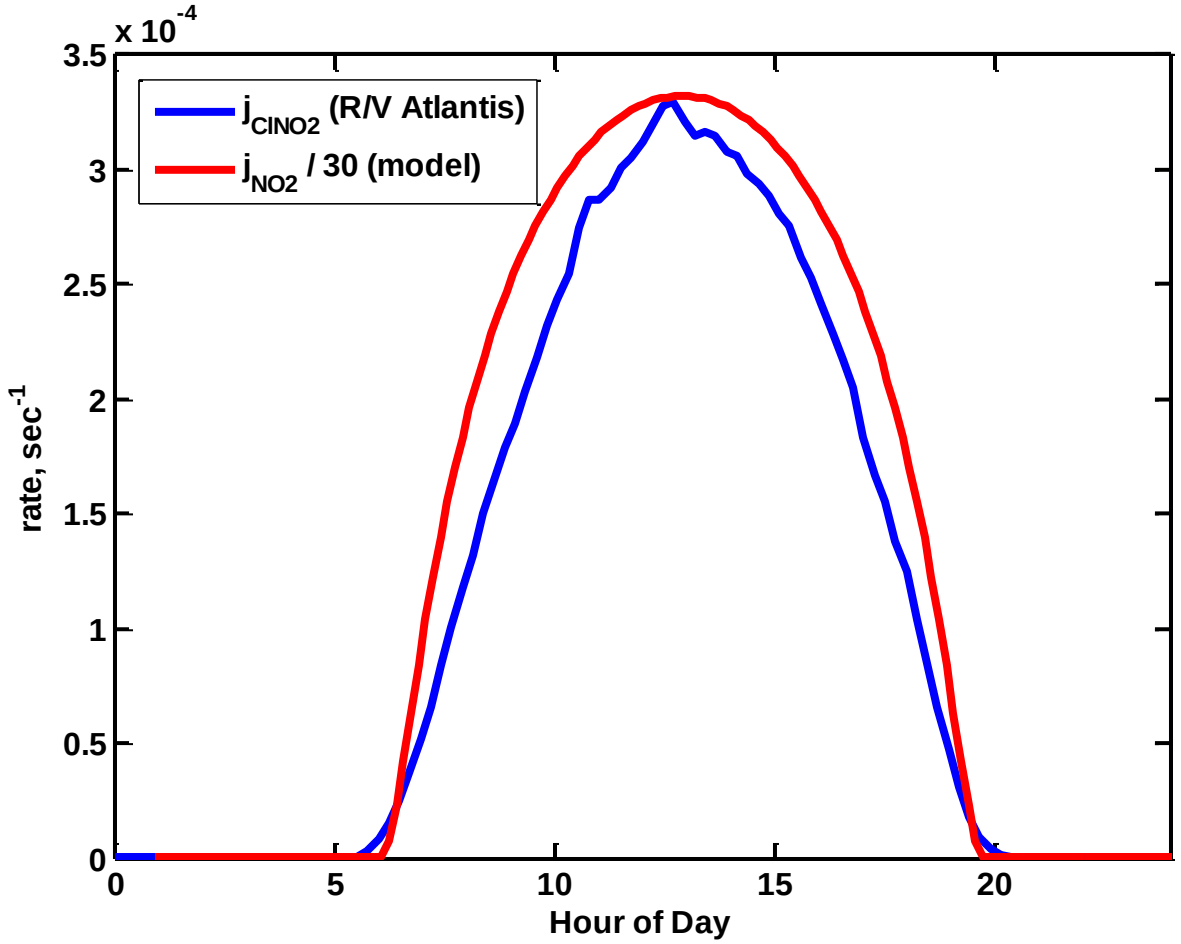

Figure S-7. Photolysis frequency comparison between j_{ClNO2} as measured aboard the R/V *Atlantis* and modeled clear sky $j_{NO2}/30$ which used in the model as a proxy for j_{ClNO2}.

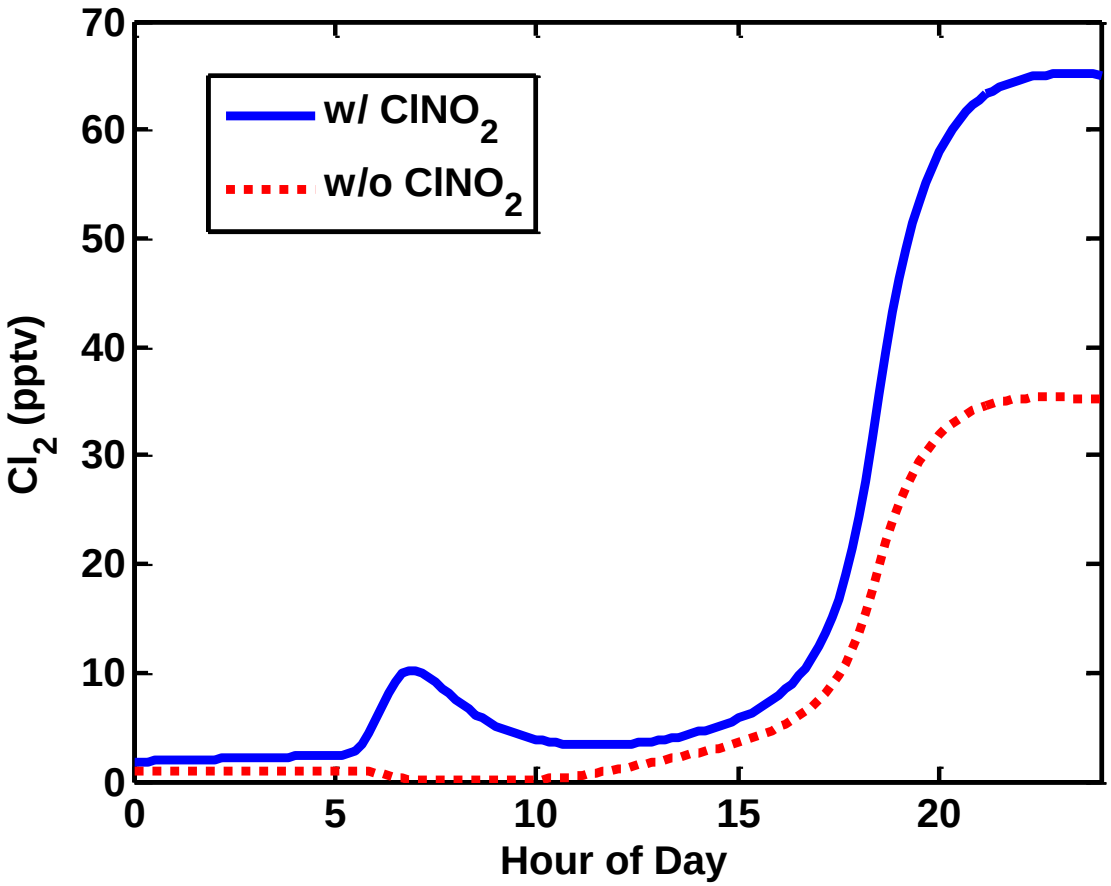

Figure S-8. Effects of $ClNO_2$ on the molecular chlorine (Cl_2) levels during a model run.

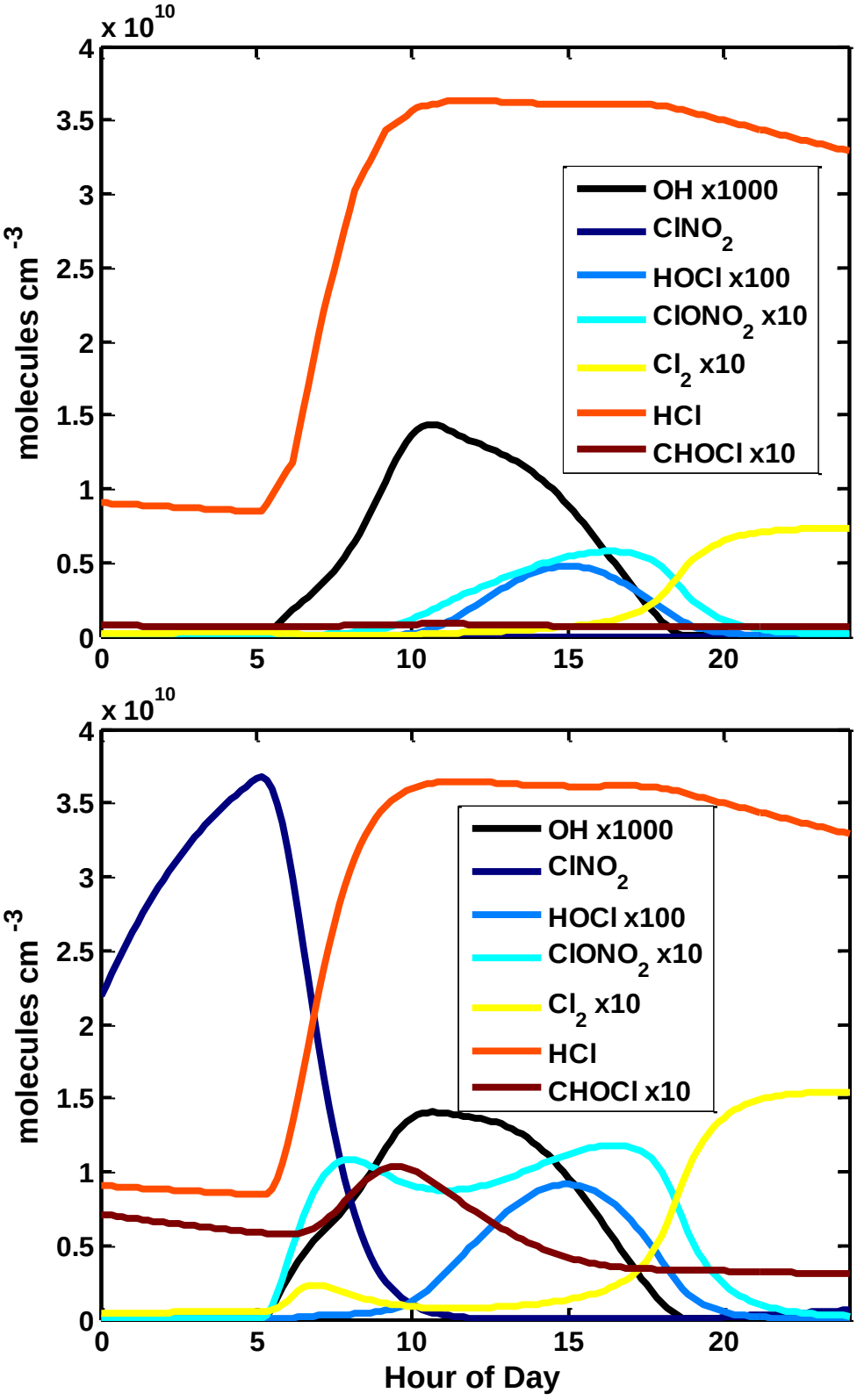

Figure S-9. Model concentrations of species relevent to chlorine atom production for the without-$ClNO_2$ (top panel) and with-$ClNO_2$ (bottom panel) model cases.

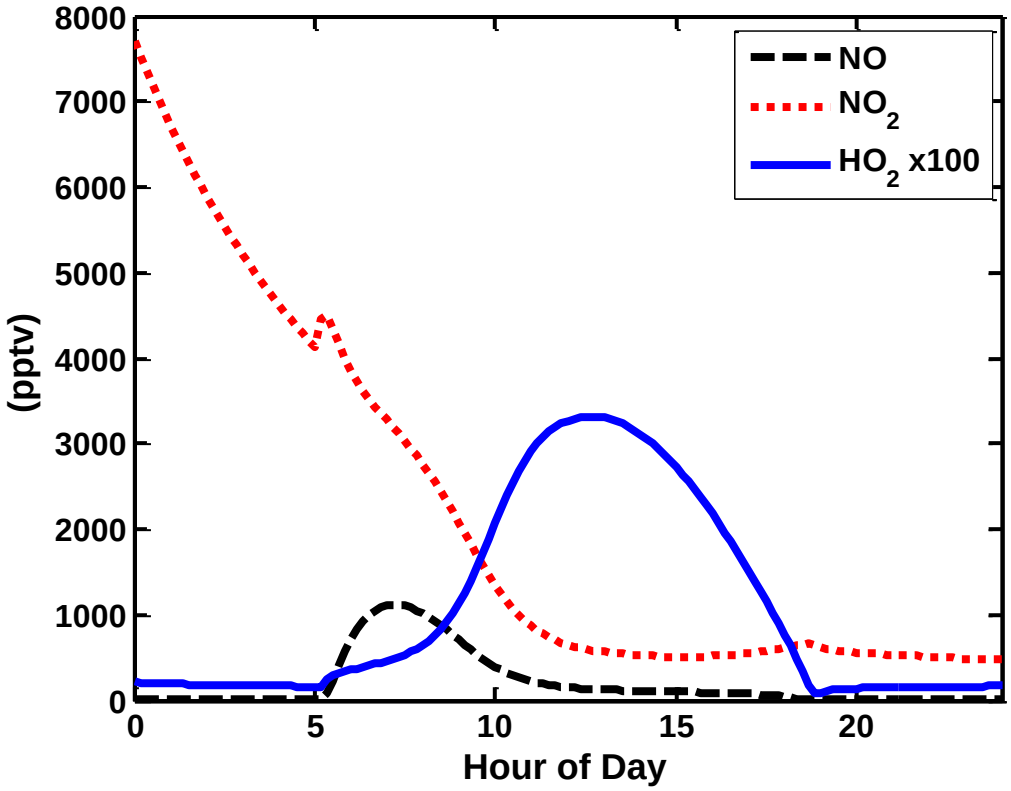

Figure S-10. Model NO, NO_2 and HO_2 mixing ratios for the with-$ClNO_2$ model case.

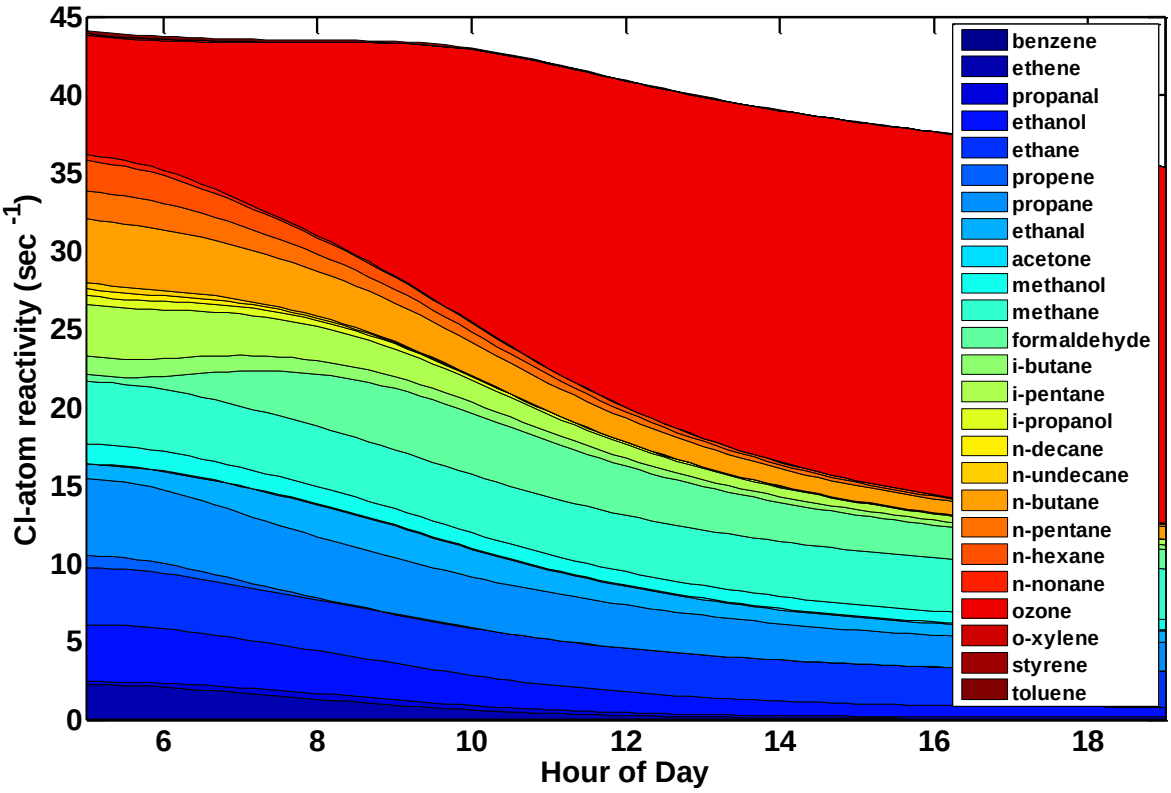

Figure S-11. Predicted Cl-atom reactivity over the course of a model day.

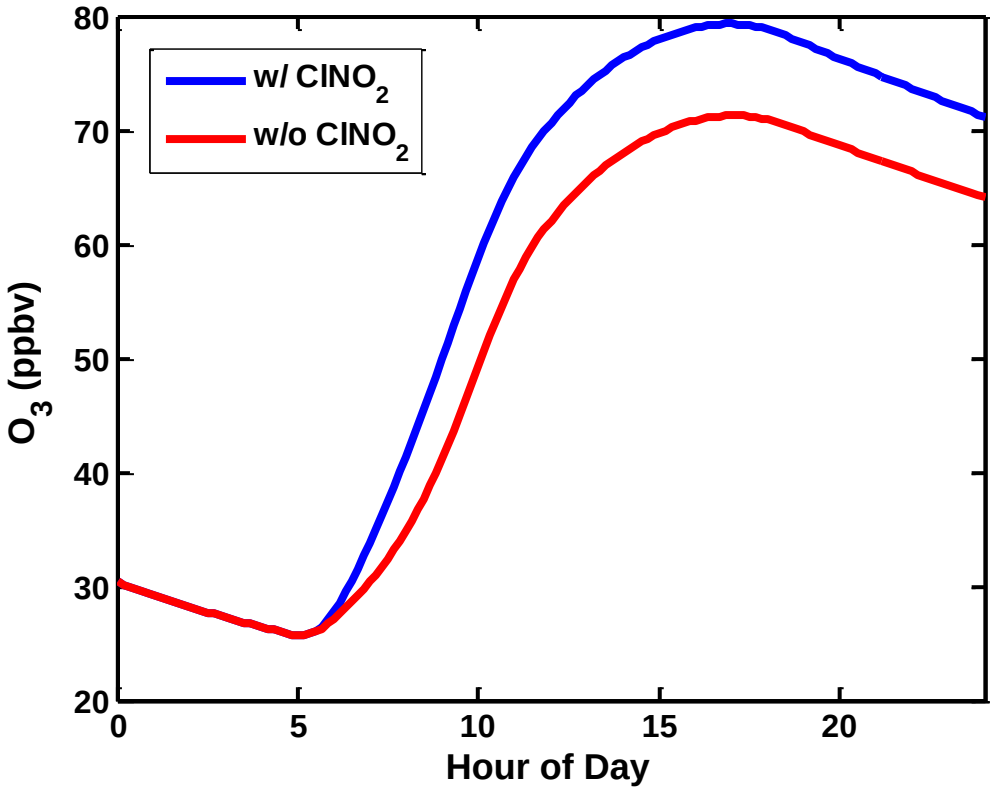

Figure S-12. Predicted O_3 mixing ratios for the with- and without-$ClNO_2$ model cases.