Supplemental Information for:

Evaluating evidence for Cl sources and oxidation chemistry in a coastal, urban environment

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Calculations of ClO and Cl concentrations

In order to estimate the concentrations of ClO and Cl in Pasadena during CalNex, the steady-state assumption was used, along with the following reactions:

$ClNO_2 + h\nu \rightarrow Cl + NO_2$ (R1)

$OH + HCl \rightarrow Cl + H_2O$ (R2)

$Cl + O_3 \rightarrow ClO + NO_2$ (R3)

$ClO + NO \rightarrow Cl + NO_2$ (R4a)

$ClO + HO_2 \rightarrow HOCl + O_2$ (R4b)

$ClO + NO_2 \rightarrow ClONO_2$ (R4c)

The calculation of steady-state ClO concentrations included reactions (R3) and (R4). For this calculation, it was assumed that the concentration of Cl was dependent solely on reactions (R1) and (R2). The calculation of Cl concentrations included reactions (R1) to (R4) and the calculated Cl reactivity described in the main text. Concentrations of OH, O_3, NO, HO_2, and NO_2, along with the photolysis rate constant for $ClNO_2$, were derived from measurements averaged over a diurnal cycle during CalNex. All bimolecular rate constants were taken from Sander et al. (2011).

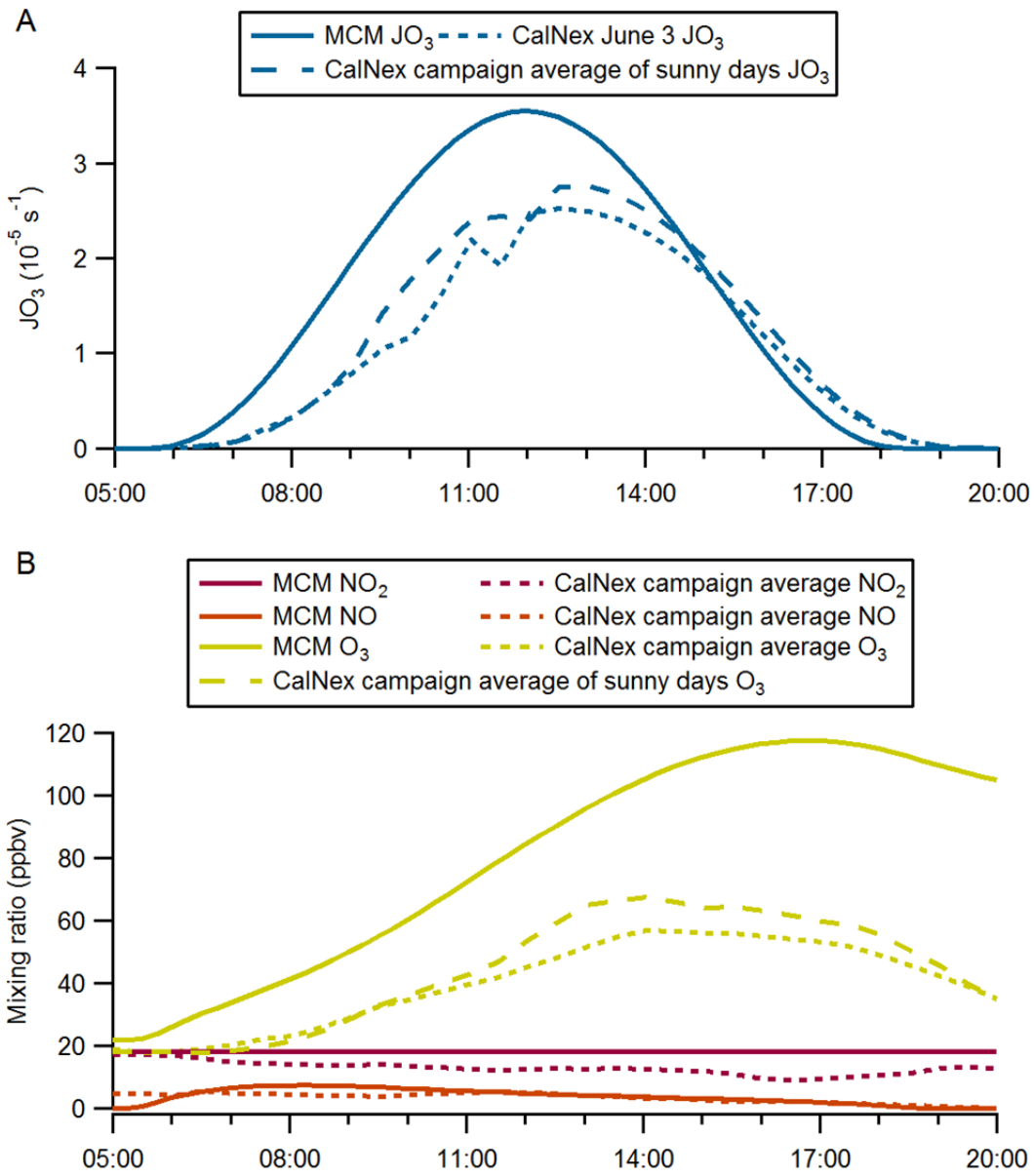

Figure S1. Comparison between concentrations calculated using AtChem with MCM (Condition set 3) and CalNex measurements for: a) J_{O3}; and b) mixing ratios of NO, NO_2, and O_3. The non-zero levels of NO and O_3 that occur simultaneously before sunrise in the measurements are a result of averaging and have no bearing on the model.

Table S1. Rate constants used for the calculation of OH and Cl reactivity at atmospheric pressure.

Compound class	Compound	OH			Cl		
		Rate constant (cm^3 $molecule^{-1}$ s^{-1})	Temp (K)	Reference*	Rate constant (cm^3 $molecule^{-1}$ s^{-1})	Temp (K)	Reference*
Alkanes	Methane	6.3E-15	298	JPL 2011	1.0E-13	298	JPL 2011
	Ethane	2.5E-13	298	JPL 2011	5.7E-11	298	JPL 2011
	Propane	1.1E-12	298	JPL 2011	1.4E-10	298	JPL 2011
	i-Butane	2.1E-12	298	IUPAC preferred value	1.40E-10	298	Beichart 1995
	n-Butane	2.3E-12	298	Atkinson 2006	2.05E-10	298	Atkinson 2006
	i-Pentane	3.6E-12	298	Atkinson 2003	1.93E-10	298	Anderson 2007
	n-Pentane	3.8E-12	298	Atkinson 2003	2.62E-10	298	Anderson 2007
	Hexane	5.2E-12	298	Atkinson 2003	3.2E-10	298	Anderson 2007
	Nonane	9.7E-12	298	Atkinson 2003	4.28E-10	296	Aschmann 1995
	Decane	1.10E-11	298	Atkinson 2003	4.87E-10	296	Aschmann 1995
	Undecane	1.23E-11	298	Atkinson 2003	*4.9E-10*		*decane*
Alcohols	Methanol	9.1E-13	298	JPL 2011	5.5E-11	298	JPL 2011
	Ethanol	3.35E-12	298	JPL 2011	1.0E-10	298	Atkinson 2006
	Isopropanol	5.5E-12	298	JPL 2011	8.6E-11	298	Atkinson 2006
Aldehydes	Formaldehyde	8.5E-12	298	JPL 2011	7.3E-11	298	JPL 2011
	Acetaldehyde	1.5E-11	298	JPL 2011	8.0E-11	298	IUPAC preferred value
	Propanal	1.9E-11	298	JPL 2011	1.3E-10	298	IUPAC preferred value
	Butanal	2.4E-11	298	Atkinson 2006	1.38E-10	298	Cuevas 2006
	Glyoxal	1.15E-11	298	JPL 2011	3.8E-11	298	Niki 1985
Ketones	Acetone	5.98E-13	298	JPL 2011	2.1E-12	298	Atkinson 2006
	2-Butanone	1.1E-12	298	IUPAC preferred value	4.0E-11	298	IUPAC preferred value
	2,3-Butadione	2.48E-13	298	Dagaut 1988	5.27E-13	298	Cuevas 2004
Aromatics	Benzene	1.2E-12	298	IUPAC preferred value	1.3E-15	295	Shi 1997
	Toluene	5.6E-12	298	IUPAC preferred value	6.2E-11	298	Wang 2005
	1,2,3-Trimethylbenzene	3.27E-11	296	Atkinson 1989	*1.E-10*		*1-ethyl benzene*
	1,2,4-Trimethylbenzene	3.25E-11	296	Atkinson 1989	*1.E-10*		*1-ethyl benzene*
	1,3,5-Trimethylbenzene	5.24E-11	298	Aschmann 2006	*1.E-10*		*1-ethyl benzene*

	1,3-Dichlorobenzene	7.21E-13	298	Wahner 1983	*1.E-15*		*benzene*
	1-Ethylbenzene	7.51E-12	298	Atkinson 1986	1.15E-10	298	Anderson 2007
	1-Ethyl-2-methylbenzene	*2.E-11*		*1-ethyl,3-methylbenzene*	*1.E-10*		*1-ethyl benzene*
	1-Ethyl-3-methylbenzene	2.12E-11	294	Colomb 2004	*1.E-10*		*1-ethyl benzene*
	Isopropylbenzene	6.61E-12	298	Ohta 1985	*1.E-10*		*1-ethyl benzene*
	n-Propylbenzene	5.71E-12	298	Atkinson 1986	*1.E-10*		*1-ethyl benzene*
	Benzaldehyde	1.26E-11	298	IUPAC preferred value	9.6E-11	295	Noziere 1994
	Styrene	4.3E-11	295	Baulch 1989	3.6E-10	295	Shi 1997
	o-Xylene	1.47E-11	298	Atkinson 1986	1.5E-10	295	Shi 1997
	m,p-Xylenes	2.45E-11	298	Atkinson 1986	1.4E-10	295	Shi 1997
Alkenes	Ethene	7.02E-12	298	JPL 2011	1.11E-10	298	JPL 2011
	Propene	1.5E-11	298	Atkinson 2006	1.34E-10	298	Atkinson 2006
	2-Methylpropene	5.1E-11	298	IUPAC preferred value	3.4E-10	298	Ezell 2002
	1-Butene	3.1E-11	298	IUPAC preferred value	3.0E-10	298	Orlando 2003
	cis-Butene	1.1E-11	298	IUPAC preferred value	3.76E-10	298	Ezell 2002
	trans-Butene	6.4E-11	298	IUPAC preferred value	4.0E-10	298	Orlando 2003
	1,3-Butadiene	6.93E-11	298	Li 2006	4.2E-10	298	Ragains 1997
Biogenics	Isoprene	1.0E-10	298	Atkinson 2006	4.3E-10	298	Orlando 2003
	Limonene	1.61E-10	298	Gill 2002	6.4E-10	298	Finlayson-Pitts 1999
	Methacrolein	2.9E-11	298	Atkinson 2006	2.35E-10	298	Orlando 2003
	Methyl vinyl ketone	2.0E-11	298	Atkinson 2006	2.2E-10	298	Orlando 2003
	α-Pinene	5.3E-11	298	Atkinson 2006	4.7E-10	298	Finlayson-Pitts 1999
	β-Pinene	7.05E-11	298	Gill 2002	5.3E-10	298	Finlayson-Pitts 1999
Acids	Hydrochloric acid	7.8E-13	298	Atkinson 2007	n/a		
	Nitric acid	1.54E-13	298	JPL 2011	<2e-16	298	JPL 2011
	Nitrous acid	4.5E-12	298	JPL 2011	n/a		
	Formic acid	4.0E-13	298	JPL 2011	2.0E-13	298	JPL 2011
Other	Hydroxyl radical (abstraction)	1.8E-12	298	JPL 2011	6.65E-16	298	Baulsch 1981
	Hydroxyl radical (addition)	6.3E-12	298	JPL 2011	n/a		

	Hydroperoxy radical	1.1E-10	298	JPL 2011	4.4E-11	298	Atkinson 2007
	Nitric oxide	7.40E-12	298	JPL 2011	1.70E-12	298	JPL 2011
	Nitrogen dioxide (1)	1.06E-11	298	JPL 2011	1.63E-11	298	JPL 2011
	Nitrogen dioxide (2)	1.79E-12	298	JPL 2011	3.59E-12	298	JPL 2011
	Ozone	7.3E-14	298	JPL 2011	1.2E-11	298	JPL 2011
	Bromoform	3.0E-14	298	JPL 2011	4.40E-13	298	JPL 2011
	Nitryl chloride	3.6E-14	298	Atkinson 2007	n/a		
	Carbon monoxide (1)	9.66E-14	298	JPL 2011	3.28E-14	298	JPL 2011
	Carbon monoxide (2)	1.40E-13	298	JPL 2011	n/a		
	DMS (abstraction)	4.7E-12	298	JPL 2011	3.5E-10	298	JPL 2011
	DMS (addition)	1.1E-41	298	JPL 2011	1.7E-10	298	JPL 2011
	Acetonitrile	2.3E-14	298	JPL 2011	1.2E-14	298	JPL 2011
	Acetylene	7.5E-13	298	JPL 2011	5.29E-11	298	JPL 2011

*If no reference available, compound of similar structure for which assumed rate constant chosen shown in reference column

Table S2. Temperature-dependent rate constants for VOCs used in tracer ratios (pressure-independent).

	OH		Cl	
Compound	Rate constant	Reference	Rate constant	Reference
Propane	$8.7\times10^{-12}\exp(615/T)$	JPL 2011	$1.45\times10^{-10}\exp(0/T)$	JPL 2011
i-Butane	$5.4\times10^{-12}\exp(-285/T)$	IUPAC preferred value	unknown	
n-Butane	$9.1\times10^{-12}\exp(-405/T)$	Atkinson 2006	$8.1\times10^{-11}\exp(-34/T)$	Atkinson 2006
Hexane	$2.54\times10^{-14}\exp(112/T)$	Atkinson 2003	unknown	
Toluene	$1.8\times10^{-12}\exp(340/T)$	IUPAC preferred value	unknown	

Table S3. Temperature-dependent rate constants for VOCs used in tracer ratios (pressure-dependent) from JPL 2011.

	OH				Cl			
Compound	k_0^{300}	k_∞^{300}	n	m	k_0^{300}	k_∞^{300}	n	m
Acetylene	5.5×10^{-30}	8.3×10^{-13}	0	-2	5.2×10^{-30}	2.2×10^{-10}	2.4	0.7

Table S4. Model conditions.

Property	Model condition
Temperature	290 K
Pressure	2.46×10^{19} molecules cm^{-3}
Water	4.2×10^{17} molecules cm^{-3}
Latitude	34.140582
Longitude	-118.122455
Date	June 1, 2010
Model start time	5:00 AM
Declination angle	Calculated by model
Photolysis rate constants	Calculated by model

Table S5. Model initial VOC concentrations for simulations.

Compound	Initial Concentration[a] (10^{10} molecule cm^{-3})	Comments
Methane	4330	
Ethane	13.9	
Propane	7.3	
n-Butane	3.2	
i-Butane	2.0	
n-Pentane	1.79	
i-Pentane	3.79	
n-Hexane	0.60	
n-Nonane	0.14	
n-Decane	0.138	
n-Undecane	0.134	
Methanol	28	
Ethanol	22	
Isopropanol	4.7	
Ethyne	2.6	
Ethene	6.13	Represents all measured alkenes: ethene, propene, butenes, butadiene, styrene, biogenic alkenes. Measured ethene 63% ofmodeled total alkenes.
Formaldehyde	7.45	Represents all measured aldehydes: C1-C4 aldehydes and benzaldehyde. Measured formaldehyde 45% of modeled total aldehydes.
Acetone	8.43	Represents all measured ketones: acetone, butanone and 2,3-butadione. Measured acetone 93% of modeled total ketones.
Toluene	1.3	Represents all measured alkyl benzenes. Measured toluene 40% of modeled total alkyl benzenes.

[a]All concentrations are diurnally-averaged pre-sunrise concentrations. Concentrations represent those of other molecules where indicated. No emissions into the model were included for any species in this table.

Table S6. Model concentrations for non-VOC species for simulations.

	Condition set 1		Condition set 2		Condition set 3	
	Concentration (molecule cm^{-3})	Comments	Concentration (molecule cm^{-3})	Comments	Concentration (molecule cm^{-3})	Comments
Nitrogen dioxide	0	Fixed	0 - 6.15×10^{11}	Fixed	4.43×10^{11}	Fixed
Nitric oxide	0	Initial	0	Initial	0	Initial
Nitrous acid	0	Initial	0	Initial	1.978×10^{10}	Initial
Ozone	5.4×10^{11}	Initial	5.4×10^{11}	Initial	5.4×10^{11}	Initial
OH	5×10^{6} - [Cl]	Fixed	0	Initial	0	Initial
Cl	5×10^{6} - [OH]	Fixed	0	Initial	0	Initial
Nitryl chloride	2.065×10^{10}	Initial	2.065×10^{10}	Initial	2.065×10^{10}	Initial
Nitrate radical	0	Fixed	0	Fixed	0	Fixed

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