

Supplemental Information for:

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

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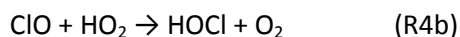
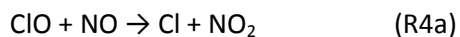
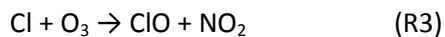
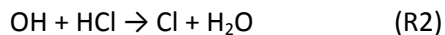
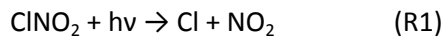
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Calculations of ClO and Cl concentrations

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:



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, O₃, NO, HO₂, and NO₂, along with the photolysis rate constant for ClNO₂, were derived from measurements averaged over a diurnal cycle during CalNex. All bimolecular rate constants were taken from Sander et al. (2011).

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

Compound class	Compound	OH			Cl		
		Rate constant ($\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$)	Temp (K)	Reference*	Rate constant ($\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$)	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		<i>decane</i>
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		<i>1-ethyl benzene</i>
	1,2,4-Trimethylbenzene	3.25E-11	296	Atkinson 1989	1.E-10		<i>1-ethyl benzene</i>
	1,3,5-Trimethylbenzene	5.24E-11	298	Aschmann 2006	1.E-10		<i>1-ethyl benzene</i>

	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).

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

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

Compound	OH				Cl			
	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% of modeled 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.

^aAll 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 x 10 ¹¹	Fixed	4.43 x 10 ¹¹	Fixed
Nitric oxide	0	Initial	0	Initial	0	Initial
Nitrous acid	0	Initial	0	Initial	1.978 x 10 ¹⁰	Initial
Ozone	5.4 x 10 ¹¹	Initial	5.4 x 10 ¹¹	Initial	5.4 x 10 ¹¹	Initial
OH	5 x 10 ⁶ - [Cl]	Fixed	0	Initial	0	Initial
Cl	5 x 10 ⁶ - [OH]	Fixed	0	Initial	0	Initial
Nitryl chloride	2.065 x 10 ¹⁰	Initial	2.065 x 10 ¹⁰	Initial	2.065 x 10 ¹⁰	Initial
Nitrate radical	0	Fixed	0	Fixed	0	Fixed

Table S7. Model concentrations of OH and Cl in Condition set 1.

OH to Cl ratio	Concentration (molecules cm ⁻³)	
	OH	Cl
0	0	5.00 x 10 ⁶
1	2.50 x 10 ⁶	2.50 x 10 ⁶
4	3.75 x 10 ⁶	1.25 x 10 ⁶
10	4.55 x 10 ⁶	4.55 x 10 ⁵
25	4.81 x 10 ⁵	1.92 x 10 ⁵
50	4.90 x 10 ⁶	9.80 x 10 ⁴
100	4.95 x 10 ⁶	4.95 x 10 ⁴
200	4.98 x 10 ⁶	2.49 x 10 ⁴
500	4.99 x 10 ⁶	9.98 x 10 ³
1000	4.995 x 10 ⁶	4.995 x 10 ³
Infinite	5.0 x 10 ⁶	0

Sources cited

- Anderson, R. S., Huang, L., Iannone, R., and Rudolph, J.: Measurements of the $^{12}\text{C}/^{13}\text{C}$ kinetic isotope effects in the gas-phase reactions of light alkanes with chlorine atoms, *J. Phys. Chem. A*, **111**, 495-504, 2007.
- Aschmann, S. M., and Atkinson, R.: Rate constants for the gas-phase reactions of alkanes with Cl atoms at 296 +/-2 K, *Int. J. Chem. Kinet.*, **27**, 613-622, 1995.
- Aschmann, S. M., Long, W. D., and Atkinson, R.: Temperature-dependent rate constants for the gas-phase reactions of OH radicals with 1,3,5-trimethylbenzene, triethyl phosphate, and a series of alkylphosphonates, *J. Phys. Chem. A*, **110**, 7393-7400, 2006.
- Atkinson, R.: Kinetics and mechanisms of the gas-phase reactions of the hydroxyl radical with organic compounds under atmospheric conditions, *Chem. Rev.*, **86**, 1986.
- Atkinson, R.: Kinetics of the gas-phase reactions of OH radicals with alkanes and cycloalkanes, *Atmos. Chem. Phys.*, **3**, 2233-2307, 2003.
- Atkinson, R., Baulch, D. L., Cox, R. A., Crowley, J. N., Hampson, R. F., Hynes, R. G., Jenkin, M. E., Rossi, M. J., and Troe, J.: Evaluated kinetic and photochemical data for atmospheric chemistry: Volume II - gas phase reactions of organic species, *Atmos. Chem. Phys.*, **6**, 3625-4055, 2006.
- Atkinson, R., Baulch, D. L., Cox, R. A., Crowley, J. N., Hampson, R. F., Hynes, R. G., Jenkin, M. E., Rossi, M. J., and Troe, J.: Evaluated kinetic and photochemical data for atmospheric chemistry: Volume III - gas phase reactions of inorganic halogens, *Atmos. Chem. Phys.*, **7**, 981-1191, 2007.
- Baulch, D. L., Duxbury, J., Grant, S. J., and Montague, D. C.: Evaluated kinetic data for high temperature reactions. Volume 4 homogeneous phase reactions of halogen- and cyanide-containing species, *J. Phys. Chem. Ref. Data*, **10**, 1981.
- Baulch, D. L., Campbell, I. M., Saunders, S. M., and Louie, P. K. K.: Rate constants for the reactions of the hydroxyl radical with indane, indene and styrene, *J. Chem. Soc. Faraday Trans. 2*, **85**, 1819-1826, 1989.
- Beichert, P., Wingen, L., Lee, J., Vogt, R., Ezell, M. J., Ragains, M. L., Neavyn, R., and Finlayson-Pitts, B. J.: Rate constants for the reactions of chlorine atoms with some simple alkanes at 298 K: measurement of a self-consistent set using both absolute and relative rate methods, *J. Phys. Chem.*, **99**, 13156-13162, 1995.
- Colomb, A., Jacob, V., Kaluzny, R., and Baussand, R.: Kinetic investigation of gas-phase reactions between the OH-radical and o-, m-, p-ethyltoluene and n-nonane in air, *Int. J. Chem. Kinet.*, **36**, 367-378, 2004.
- Cuevas, C. A., Notario, A., Martinez, E., and Albaladejo, J.: Temperature-dependence study of the gas-phase reactions of atmospheric Cl atoms with a series of aliphatic aldehydes, *Atmos. Environ.*, **40**, 3845-3854, 2006.
- Dagaut, P., Wallington, T. J., Liu, R., and Kurylo, M. J.: A kinetics investigation of the gas-phase reactions of OH radicals with cyclic ketones and diones: mechanistic insights, *J. Phys. Chem.*, **92**, 1988.

Ezell, M. J., Wang, W., Ezell, A. A., Soskin, G., and Finlayson-Pitts, B. J.: Kinetics of reactions of chlorine atoms with a series of alkenes at 1 atm and 298 K, *Phys. Chem. Chem. Phys.*, 2002, 5813-5820, 2002.

Finlayson-Pitts, B. J., Keoshian, C. J., Buehler, B., and Ezell, A. A.: Kinetics of reaction of chlorine atoms with some biogenic organics, *Int. J. Chem. Kinet.*, 31, 491-499, 1999.

Gill, K. J., and Hites, R. A.: Rate constants for the gas-phase reactions of the hydroxyl radical with isoprene, α - and β -pinene, and limonene as a function of temperature, *J. Phys. Chem. A*, 106, 2538-2544, 2002.

Li, Z. J., Nguyen, P., de Leon, M. F., Wang, J. H., Han, K. L., and He, G. Z.: Experimental and theoretical study of reaction of OH with 1,3-butadiene, *J. Phys. Chem. A*, 110, 2698-2708, 2006.

Niki, H., Maker, P. D., Savage, C. M., and Breitenbach, L. P.: An FTIR study of the Cl-atom-initiated reaction of glyoxal, *Int. J. Chem. Kinet.*, 17, 1985.

Noziere, B., Lesclaux, R., Hurley, M. D., Dearth, M. A., and Wallington, T. J.: A kinetic and mechanistic study of the self-reaction and reaction with HO₂ of the benzylperoxy radical, *J. Phys. Chem.*, 98, 2864-2873, 1994.

Ohta, T., and Ohyama, T.: A set of rate constants for the reaction of OH radicals with aromatic hydrocarbons, *Bull. Chem. Soc. Jpn.*, 58, 1985.

Orlando, J. J., Tyndall, G. S., Apel, E. C., Riemer, D. D., and Paulson, S. E.: Rate coefficients and mechanisms of the reaction of Cl-atoms with a series of unsaturated hydrocarbons under atmospheric conditions, *Int. J. Chem. Kinet.*, 35, 334-353, 2003.

Ragains, M. L., and Finlayson-Pitts, B. J.: Kinetics and mechanism of the reaction of Cl atoms with 2-methyl-1,3-butadiene (isoprene) at 298 K, *J. Phys. Chem. A*, 101, 1509-1517, 1997.

Sander, S. P., Friedl, R. R., Abbatt, J. P. D., Barker, J. R., Burkholder, J. B., Golden, D. M., Kolb, C. E., Kurylo, M. J., Moortgat, G. K., Wine, P. H., Huie, R. E., and Orkin, V. L.: Chemical kinetics and photochemical data for use in atmospheric studies: Evaluation number 17, Jet Propulsion Laboratory, Pasadena, 2011.

Shi, J., and Bernhard, M. J.: Kinetic studies of Cl-atom reactions with selected aromatic compounds using the photochemical reactor-FTIR spectroscopy technique, *Int. J. Chem. Kinet.*, 29, 349-358, 1997.

Wahner, A., and Zetzsch, C.: Rate constants for the addition of OH to aromatics (benzene, p-chloroaniline, and o-, m-, and p-dichlorobenzene) and the unimolecular decay of the adduct. Kinetics into a quasi-equilibrium., *J. Phys. Chem.*, 87, 1983.

Wang, L., Arey, J., and Atkinson, R.: Reactions of chlorine atoms with a series of aromatic hydrocarbons, *Environ. Sci. Technol.*, 39, 5302-5310, 2005.