Supplementary Material: Computer Kinetics Modeling

("Enhanced Surface Photochemistry in Chloride-Nitrate Ion Mixtures", Wingen et al.)

A model consisting of 167 gas phase reactions was developed to assess the impact of secondary chemistry in the gas phase on the measured NO_2 concentrations. In addition, it was used to probe sources of gas phase OH in order to assess whether the increased photochemical production of OH from reaction (1a) which accompanies the NO_2 is significant in this system.

The production of gas phase NO_2 from the surface nitrate ion photolysis (1a) was parameterized by matching the model to experimental NO_2 data from pure $NaNO_3$ photolysis experiments. The channel producing nitrite ion and O atoms (reaction 1b) was then assigned a rate constant based on the known relative quantum yields for the two channels.[1, 2]

In addition to the aerosol photolysis experiments described in the main text, experiments were also carried out with the addition of a mixture of alkanes. Alkane experiments were carried out using propane, butane, and isobutane gases in the presence of nebulized aerosol from similar $NaCl:NaNO_3$ molar ratios. The relative rates of loss of propane, butane and isobutane are sensitive indicators of OH versus chlorine atom chemistry.[3] In pure $NaNO_3$ photolysis experiments with alkanes present, the slope of a plot of the natural logarithm of the ratios butane/propane versus isobutane/propane at various times during photolysis was 1.28 ± 0.03 (2s), in good agreement with the calculated slope (1.23) based on the published rate constants for OH with these alkanes.[4] This confirms that OH is primarily responsible for the alkane destruction during photolysis of pure $NaNO_3$, as expected.

There are a number of possible sources of OH in this system: (1) nitrate photolysis (1a); (2) formation of O_3 from the NO_2 photolysis and its photochemistry to generate $O(^1D)$ which reacts with water vapor to generate OH;[5] and (3) the RO_2/HO_2 - NO_x photochemical cycle which also leads to more OH production.[5] Application of the model shown in Table S-1 showed that the $O(^1D)$ reaction with water vapor was the major source of OH in the gas phase, and that OH from NO_3^- photolysis would contribute at most only ~ 5% for the 9:1 NaCl:$NaNO_3$ case.

Another possible source of OH radicals in this system is the photolysis of HONO which was reported recently from NO_2 absorption of light at $\lambda > 420$ nm. This forms excited state, NO_2^*, which then reacts with water to form HONO and OH.[6] The lamps used in the current studies have a broad emission from 270 – 380 nm with several narrow emission lines above 420 nm. Therefore, in separate experiments NO_2 was continuously added to a Teflon® chamber at a rate chosen to mimic NO_2 formation from NO_3^- photolysis. The chamber also contained the mixture of alkanes in air at ~90% RH, but no aerosol. During a 3.3 h irradiation, each alkane decreased by ~13 – 15%. In comparison, typical aerosol photolysis experiments with alkanes resulted in alkane destruction of 30 – 70% over the same time period. The decay of alkanes observed in aerosol photolysis experiments was therefore due to OH formed primarily by processes other than the NO_2^*-H_2O reaction. This experiment also rules out formation of HONO from NO_2 hydrolysis as a significant process in this system.

Modeling pure $NaNO_3$ experiments with and without alkanes established vital constraints for NO_2 and OH production rates within the model. For example, the rate of OH production strongly influenced the time evolution of NO_2 because of the removal of NO_2 by the OH reaction to form HNO_3. The experimental alkane decay rate was modeled to provide the total OH production rate, which in turn constrained the rate constant for NO_2 production from NO_3^- photolysis. Thus, using the experimental alkane decay rate to fix the rate of OH production, the net NO_2 production rate was constrained when alkanes were absent. The pure $NaNO_3$ model also established a starting point for modeling the mixtures containing both NO_3^- and Cl^-.

The possibility of production of gaseous chlorine atom precursors in the mixed chloride-nitrate cases must be considered. For example, OH oxidation of chloride ions in the bulk and at interfaces to generate gaseous Cl_2 is well known.[7-9] Such reactions were parameterized by including a reaction that generated gaseous Cl atoms with a rate constant $k_{Cl(g)}$. Addition of gas phase chlorine chemistry to the kinetics model involved adding well-known gas phase reactions available from the literature. Similar to the $NaNO_3$ modeling, alkane decay rates in the mixed aerosol experiments were used to probe for a contribution of chlorine atoms. The rate constants for Cl and OH production, $k_{Cl(g)}$ and $k_{OH(g)}$, were adjusted to match the decay of alkanes and held constant when fitting NO_2 production in experiments without alkanes. These constraints in the mixed aerosol models provided by alkane experiments provided insight into the relative concentrations of Cl and OH and their effect on the net NO_2 production. In all cases, the gas phase chlorine atom concentration was estimated to be less than ~ 1% of that of OH when alkanes were present. However, as discussed in the text, nitrogen halogen compounds such as $ClNO_2$ may contribute to the measured NO_y at longer reaction times under the experimental conditions used to measure the NO_2 enhancement.

Table S-1. List of reactions and rate constants used in kinetics modeling program.

A. Nitrogen oxide chemistry and photochemistry

1.	NO_3^-	+	hυ	→	NO_2					1.0×10^{-7} [a]
2.	NO_3^-	+	hυ	→	nitrite	+	O			1.0×10^{-8} [b]
3.	NO_3^- (& NO_2^-)	+	hυ	→	OH					2.0×10^{-9} [c]
4.	NO_2^-	+	hυ	→	NO					1.0×10^{-6} [d]
5.	NO_2	+	hυ	→	NO	+	O			6.8×10^{-4} [e]
6.	HNO_3	+	hυ	→	OH	+	NO_2			5.35×10^{-6} [j]
7.	HONO	+	hυ	→	OH	+	NO			1.45×10^{-4} [j]
8.	O_3	+	hυ	→	O_2	+	$O(^1D)$			8.0×10^{-4} [e,j]
9.	O_3	+	hυ	→	O_2	+	O			8.9×10^{-5} [e,j]
10.	O_3	+	NO	→	NO_2	+	O_2			1.9×10^{-14} [f]
11.	O_3	+	NO_2	→	NO_3	+	O_2			3.2×10^{-17} [f]
12.	O_3	+	HONO	→	O_2	+	HNO_3			5.0×10^{-19} [f]
13.	OH	+	NO_2	→	HNO_3					1.0×10^{-11} [g]
14.	OH	+	O_3	→	HO_2	+	O_2			7.3×10^{-14} [f]
15.	OH	+	H_2O_2	→	HO_2	+	H_2O			1.8×10^{-12} [f]
16.	OH	+	OH	→	H_2O	+	O			1.8×10^{-12} [f]
17.	OH	+	OH	→	H_2O_2					6.3×10^{-12} [g]
18.	OH	+	HO_2	→	H_2O	+	O_2			1.1×10^{-10} [f]
19.	OH	+	H_2	→	H_2O	+	H			6.7×10^{-15} [f]
20.	OH	+	NO_2	→	HOONO					1.7×10^{-12} [g]
21.	OH	+	NO_3	→	HO_2	+	NO_2			2.2×10^{-11} [f]
22.	OH	+	HONO	→	H_2O	+	NO_2			4.5×10^{-12} [f]
23.	OH	+	HNO_3	→	H_2O	+	NO_3			1.5×10^{-13} [f]
24.	OH	+	HO_2NO_2	→	products					4.6×10^{-12} [f]
25.	H	+	O_2	→	HO_2					9.2×10^{-13} [g]
26.	H	+	O_3	→	OH	+	O_2			2.9×10^{-11} [f]
27.	NO_3	+	NO_2	→	N_2O_5					1.2×10^{-12} [g]
28.	NO_3	+	NO_2	→	NO	+	NO_2			6.6×10^{-16} [f]
29.	NO	+	NO_3	→	NO_2	+	NO_2			2.6×10^{-11} [f]
30.	N_2O_5			→	NO_3	+	NO_2			4.0×10^{-2} [f]
31.	NO_3	+	NO_3	→	NO_2	+	NO_2	+	O_2	2.3×10^{-16} [f]
32.	N_2O_5	+	H_2O	→	HNO_3	+	HNO_3			2×10^{-2} [f]
33.	HOONO			→	OH	+	NO_2			7.7×10^{-1} [f]
34.	HO_2NO_2			→	HO_2	+	NO_2			6.9×10^{-2} [f]
35.	HO_2	+	NO	→	HNO_3					1.0×10^{-11} [g]
36.	HO_2	+	NO_2	→	HO_2NO_2					1.1×10^{-12} [g]
37.	HO_2	+	NO_2	→	HONO	+	O_2			5×10^{-16} [f]
38.	HO_2	+	NO_3	→	OH	+	NO_2			3.5×10^{-12} [f]
39.	HO_2	+	O_3	→	OH	+	O_2			1.9×10^{-15} [f]
40.	HO_2	+	HO_2	→	H_2O_2	+	O_2			2.7×10^{-12} [f]
41.	H	+	HO_2	→	OH	+	OH			7.2×10^{-11} [f]

42.	H	+	HO_2	→	O	+	H_2O	1.6×10^{-12} [f]
43.	H	+	HO_2	→	H_2	+	O_2	6.9×10^{-12} [f]
44.	H	+	NO_2	→	OH	+	NO	1.3×10^{-10} [f]
45.	O	+	N_2O_5	→	products			3.0×10^{-16} [f]
46.	O	+	HNO_3	→	OH	+	NO_3	3.0×10^{-17} [f]
47.	O	+	HO_2NO_2	→	products			8.6×10^{-16} [f]
48.	O	+	OH	→	O_2	+	H	3.3×10^{-11} [f]
49.	O	+	HO_2	→	OH	+	O_2	5.9×10^{-11} [f]
50.	O	+	H_2O_2	→	OH	+	HO_2	1.7×10^{-15} [f]
51.	O	+	O_2	→	O_3			1.5×10^{-14} [f]
52.	O	+	NO_2	→	NO	+	O_2	1.04×10^{-11} [f]
53.	O	+	O_3	→	O_2	+	O_2	8.0×10^{-15} [f]
54.	O	+	NO	→	NO_2			1.6×10^{-12} [g]
55.	O	+	NO_3	→	NO_2	+	O_2	1.0×10^{-11} [f]
56.	O	+	NO_2	→	NO_3			3.3×10^{-12} [f]
57.	$O(^1D)$	+	O_2	→	O	+	O_2	3.95×10^{-11} [f]
58.	$O(^1D)$	+	O_3	→	O_2	+	O_2	1.2×10^{-10} [f]
59.	$O(^1D)$	+	O_3	→	O	+	O + O_2	1.2×10^{-10} [f]
60.	$O(^1D)$	+	H_2	→	OH	+	H	1.1×10^{-10} [f]
61.	$O(^1D)$	+	N_2	→	O	+	N_2	3.1×10^{-11} [f]
62.	$O(^1D)$	+	N_2	→	N_2O			6.89×10^{-17} [g]
63.	$O(^1D)$	+	H_2O	→	OH	+	OH	2.0×10^{-10} [f]
64.	$O(^1D)$	+	N_2O	→	N_2	+	O_2	5.0×10^{-11} [f]
65.	$O(^1D)$	+	N_2O	→	NO	+	NO	6.7×10^{-11} [f]
66.	$O(^1D)$	+	CO_2	→	O	+	CO_2	1.1×10^{-10} [f]
67.	$O(^1D)$	+	HCl	→	O	+	HCl	1.35×10^{-11} [f]
68.	$O(^1D)$	+	HCl	→	H	+	ClO	3.6×10^{-11} [f]
69.	$O(^1D)$	+	HCl	→	OH	+	Cl	1.01×10^{-10} [f]
70.	$O(^1D)$	+	Cl_2	→	O	+	Cl_2	6.75×10^{-11} [f]
71.	$O(^1D)$	+	Cl_2	→	ClO	+	Cl	2.03×10^{-10} [f]
72.	OH	+	NO	→	HONO			7.3×10^{-12} [g]
73.	HNO_3	+	NO_2	→	OH	+	NO + NO	1.2×10^{-18} [k]
74.	HNO_3			→	wall			3×10^{-4} [h]

B. Chlorine chemistry and photochemistry

75.	Cl^-			→	Cl			9.0×10^{-9} [i]
76.	Cl_2	+	$h\upsilon$	→	Cl	+	Cl	4.59×10^{-4} [j]
77.	ClNO	+	$h\upsilon$	→	Cl	+	NO	3.25×10^{-4} [j]
78.	$ClNO_2$	+	$h\upsilon$	→	Cl	+	NO_2	3.03×10^{-4} [j]
79.	$ClONO_2$	+	$h\upsilon$	→	Cl	+	NO_3	5.36×10^{-5} [j]
80.	$ClONO_2$	+	$h\upsilon$	→	ClO	+	NO_2	3.41×10^{-5} [j]
81.	ClOO	+	$h\upsilon$	→	ClO	+	O	7.38×10^{-4} [j]
82.	HOCl	+	$h\upsilon$	→	OH	+	Cl	1.32×10^{-4} [j]
83.	ClO	+	O_3	→	ClOO	+	O_2	1.4×10^{-17} [f]

84.	ClO	+	O_3	→	OClO	+	O_2	1.0×10^{-18}[f]
85.	ClO	+	H_2	→	products			1.0×10^{-19}[f]
86.	ClO	+	NO	→	NO_2	+	Cl	1.7×10^{-17}[f]
87.	ClO	+	NO_2	→	$ClONO_2$			2.3×10^{-12}[g]
88.	ClO	+	NO_3	→	ClOO	+	NO_2	4.7×10^{-13}[f]
89.	ClO	+	ClO	→	Cl_2	+	O_2	4.8×10^{-15}[f]
90.	ClO	+	ClO	→	ClOO	+	Cl	8.0×10^{-15}[f]
91.	ClO	+	ClO	→	OClO	+	Cl	3.5×10^{-15}[f]
92.	Cl	+	ClOO	→	Cl_2	+	O_2	2.3×10^{-10}[f]
93.	Cl	+	ClOO	→	ClO	+	ClO	1.2×10^{-11}[f]
94.	Cl	+	Cl_2O	→	Cl_2	+	ClO	9.6×10^{-11}[f]
95.	Cl	+	Cl_2O_2	→	products			1.0×10^{-10}[f]
96.	Cl	+	ClNO	→	NO	+	Cl_2	8.1×10^{-11}[f]
97.	Cl	+	$ClONO_2$	→	Cl_2	+	NO_3	1.0×10^{-11}[f]
98.	O	+	ClO	→	Cl	+	O_2	3.7×10^{-11}[f]
99.	O	+	OClO	→	ClO	+	O_2	1.0×10^{-13}[f]
100.	O	+	OClO	→	ClO_3			2.3×10^{-12}[g]
101.	O	+	Cl_2O	→	ClO	+	ClO	4.5×10^{-12}[f]
102.	O	+	$ClONO_2$	→	products			2.0×10^{-13}[f]
103.	O	+	HOCl	→	OH	+	ClO	1.7×10^{-13}[f]
104.	O	+	HCl	→	OH	+	Cl	1.5×10^{-16}[f]
105.	O_3	+	OClO	→	products			3.0×10^{-19}[f]
106.	OH	+	Cl_2	→	HOCl	+	Cl	6.7×10^{-14}[f]
107.	OH	+	ClO	→	Cl	+	HO_2	1.8×10^{-11}[f]
108.	OH	+	ClO	→	HCl	+	O_2	1.3×10^{-12}[f]
109.	OH	+	OClO	→	HOCl	+	O_2	6.8×10^{-12}[f]
110.	OH	+	$ClNO_2$	→	HOCl	+	NO_2	3.6×10^{-14}[f]
111.	OH	+	$ClONO_2$	→	products			3.9×10^{-13}[f]
112.	OH	+	HOCl	→	H_2O	+	ClO	5.0×10^{-13}[f]
113.	OH	+	HCl	→	H_2O	+	Cl	8.0×10^{-13}[f]
114.	HO_2	+	Cl	→	HCl	+	O_2	3.2×10^{-11}[f]
115.	HO_2	+	Cl	→	OH	+	ClO	9.1×10^{-12}[f]
116.	HO_2	+	ClO	→	HOCl	+	O_2	5.6×10^{-12}[f]
117.	NO	+	OClO	→	NO_2	+	ClO	3.4×10^{-13}[f]
118.	Cl	+	O_3	→	ClO	+	O_2	1.2×10^{-11}[f]
119.	Cl	+	NO	→	ClNO			1.9×10^{-12}[g]
120.	Cl	+	NO_2	→	$ClNO_2$			3.5×10^{-12}[g]
121.	Cl	+	NO_3	→	ClO	+	NO_2	2.4×10^{-11}[f]
122.	Cl	+	HNO_3	→	products			2.0×10^{-16}[f]
123.	Cl	+	O_2	→	ClOO			5.2×10^{-14}[g]
124.	ClOO			→	Cl	+	O_2	1.79×10^{7}[f]
125.	Cl	+	HOCl	→	HCl	+	ClO	8.0×10^{-13}[f]
126.	Cl	+	HOCl	→	OH	+	Cl_2	8.0×10^{-13}[f]
127.	HNO_3	+	Cl^-	→	NO_3^-	+	HCl	1×10^{-14}[l]

C. Alkane reactions with OH and Cl

128.	C_3H_8	+	OH	→	proO$_2$	+	H_2O	1.12×10^{-12} [f]
129.	i-C_4H_{10}	+	OH	→	t-butO$_2$	+	H_2O	2.19×10^{-12} [f]
130.	n-C_4H_{10}	+	OH	→	i-butO$_2$	+	H_2O	2.44×10^{-12} [f]
131.	C_3H_8	+	Cl	→	proO$_2$	+	H_2O	1.37×10^{-10} [f]
132.	i-C_4H_{10}	+	Cl	→	t-butO$_2$	+	H_2O	1.43×10^{-10} [f]
133.	n-C_4H_{10}	+	Cl	→	i-butO$_2$	+	H_2O	2.18×10^{-10} [f]
134.	proO$_2$	+	proO$_2$	→	proOH	+	O_2	8.0×10^{-15}
135.	proO$_2$	+	proO$_2$	→	acetone	+	O_2	8.0×10^{-15}
136.	proO$_2$	+	proO$_2$	→	proO	+	O_2	2.4×10^{-14}
137.	proO$_2$	+	NO	→	proONO$_2$			3.80×10^{-13}
138.	proO$_2$	+	NO	→	proO	+	NO_2	8.66×10^{-12}
139.	proO$_2$	+	HO_2	→	proOOH	+	O_2	1.19×10^{-11}
140.	proO$_2$	+	NO_3	→	proO	+	NO_2	2.5×10^{-12}
141.	proO	+	O_2	→	acetone	+	HO_2	8.0×10^{-15}
142.	proO	+	NO_2	→	proONO$_2$			3×10^{-11}
143.	t-butO$_2$	+	t-butO$_2$	→	t-butOH	+	O_2	2.01×10^{-15}
144.	t-butO$_2$	+	t-butO$_2$	→	t-butO	+	O_2	4.69×10^{-15}
145.	t-butO$_2$	+	NO	→	t-butONO$_2$			2.13×10^{-13}
146.	t-butO$_2$	+	NO	→	tbutO	+	NO_2	8.3×10^{-12}
147.	t-butO$_2$	+	HO_2	→	t-butOOH	+	O_2	1.43×10^{-11}
148.	t-butO$_2$	+	NO_3	→	t-butO	+	NO_2	2.5×10^{-12}
149.	t-butO			→	acetone	+	CH_3OO	787.5
150.	CH_3OO	+	O_2	→	CH_3OH			2.46×10^{-13}
151.	CH_3OO	+	O_2	→	HCHO			2.46×10^{-13}
152.	CH_3OO	+	NO	→	CH_3ONO_2			7.7×10^{-15}
153.	CH_3OO	+	NO	→	CH_3O	+	NO_2	2.4×10^{-13}
154.	CH_3OO	+	HO_2	→	CH_3OOH	+	O_2	5.2×10^{-12}
155.	CH_3OO	+	NO_3	→	CH_3O	+	NO_2	1×10^{-12}
156.	CH_3O	+	O_2	→	HCHO	+	HO_2	2.0×10^{-15}
157.	HCHO	+	OH	→	HO_2	+	CO_2	9.37×10^{-12}
158.	t-butO	+	NO_2	→	t-butONO$_2$			3×10^{-11}
159.	i-butO$_2$	+	i-butO$_2$	→	i-butOH	+	O_2	5.0×10^{-14}
160.	i-butO$_2$	+	i-butO$_2$	→	i-butanone	+	O_2	5.0×10^{-14}
161.	i-butO$_2$	+	i-butO$_2$	→	i-butO	+	O_2	1.5×10^{-13}
162.	i-butO$_2$	+	NO	→	i-butONO$_2$			7.65×10^{-13}
163.	i-butO$_2$	+	NO	→	i-butO	+	NO_2	7.7×10^{-12}
164.	i-butO$_2$	+	HO_2	→	i-butOOH	+	O_2	1.4×10^{-11}
165.	i-butO$_2$	+	NO_3	→	i-butO	+	NO_2	2.5×10^{-12}
166.	i-butO	+	O_2	→	i-butanone	+	HO_2	7.67×10^{-15}
167.	i-butO	+	NO_2	→	i-butONO$_2$			3×10^{-11}

a Obtained by matching NO_2 production from pure $NaNO_3$. This value was varied as the Cl^-:NO_3^- ratio changed.
b Based on published quantum yields, this channel of nitrate photolysis is 10 times slower.
c Represents the gas phase OH production by NO_3^- (and NO_2^-) photolysis. The rate constant was obtained by matching the model to the measured decay of alkanes in a pure $NaNO_3$ experiment. The value varied as the Cl^-:NO_3^- ratio changed.
d Nitrite photolysis produces both NO and OH approximately 10 times faster than NO_3^- photolysis at the wavelengths used here.[1]
e Measured experimentally (see text).
f From JPL publication 06-2.
g Termolecular rate constants were calculated using M = 760 Torr based on data from JPL publication 06-2.
h Estimated wall loss of HNO_3.
i Obtained by matching the decay of alkanes in experiments containing mixtures of Cl^- and NO_3^-. This value was varied as the Cl^-:NO_3^- ratio changed.
j Calculated based on the measured k_p for NO_2 over the range 240 – 450 nm from cross sections and quantum yields available in JPL publication as well as our own UVB lamp intensity data. For example, k_p^{HONO} was calculated from

$$\frac{k_p^{HONO}}{k_p^{NO_2}} = \frac{\int_{240nm}^{450nm} \Phi_{HONO}(\lambda)\sigma_{HONO}(\lambda)F(\lambda)d\lambda}{\int_{240nm}^{450nm} \Phi_{NO_2}(\lambda)\sigma_{NO_2}(\lambda)F(\lambda)d\lambda}$$

k Rate constant for heterogeneous conversion of an HNO_3-NO_2 surface complex to NO, estimated based on the formation of NO in pure NO_3^- photolysis experiments.
l Estimated; replacement of Cl^- by NO_3^-.

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