

***Supplement for***

**Summertime photochemistry during CAREBeijing-2007: RO<sub>x</sub> budgets and O<sub>3</sub> formation**

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The supplement information includes: 1) more detailed descriptions of instruments and experimental methods; 2) additional descriptions for the model including: the aromatics oxidation mechanism used in the 1-D REAM model; VOC model input; and estimation of model errors.

## 1 **Descriptions of instruments and experimental methods**

2 **O<sub>3</sub> and CO measurements.** O<sub>3</sub> and CO were measured with commercial instruments  
3 (ECOTECH, EC9810 and EC9830). The EC9810 Ozone Analyzer combines microprocessor control  
4 with ultraviolet (UV) photometry to measure O<sub>3</sub> with a detection limit of 0.5 ppbv. The EC9830  
5 series of Carbon Monoxide analyzers use NDIR gas filter correlation photometry to measure  
6 Carbon Monoxide (CO). Zero signals were routinely measured every 2 hours by supplying dry  
7 purified air into the sample line. We note that as water vapor interferes the CO analyzer, using dry  
8 air will give lower baseline values, thus higher CO concentration. The uncertainties for these  
9 measurements are estimated to be 5% (1 standard deviation, and so for all other uncertainties).

10 **NO and NO<sub>y</sub> measurements.** NO mixing ratios were measured with a custom  
11 chemiluminescence detector (*SI*). The instrument was calibrated periodically (2–4 hours) by a  
12 standard addition of a known amount of nitric oxide. Background levels were obtained periodically  
13 (30 minutes) by switching the sampled flow through a pre-reactor. NO<sub>y</sub> levels were measured by  
14 use of a molybdenum converter operated at 300°C. The sample flow to the NO detector was  
15 periodically switched between ambient and the converter by a three way Teflon valve. NO<sub>y</sub>  
16 conversion levels were estimated to be greater than 97% for NO<sub>2</sub>. The conversion efficiency for  
17 NO<sub>2</sub> were examined before and after the campaign and appears to be quantitative i.e. > 95%. The  
18 conversion efficiency for HNO<sub>3</sub> was found to be greater than 85% after the mission. We did not  
19 look at anything in Beijing during the measurements, as we didn't have the ability to do so. High  
20 conversion efficiency for PAN (greater than 95%) can be expected because PAN will decompose to  
21 NO<sub>2</sub> readily at high temperature. The efficiency for NO should be comparable with NO<sub>2</sub>, too.  
22 Organic nitrates were probably close to 100% converted. The uncertainties for NO and NO<sub>y</sub>  
23 measurements are estimated to be 5% and 10%, respectively.

24 **PAN measurements.** Peroxyacetyl nitrate (PAN) were measured using a chemical  
25 ionization mass spectrometer (CIMS) (*S2, S3*). The instrument was calibrated periodically with a  
26 photolytic PAN source and the background response of the instrument was determined by  
27 periodically scrubbing sampled air through hot stainless steel tubing (200 °C) (*S4*). The sensitivity  
28 of the instrument was found to decrease at high NO<sub>x</sub> levels. High levels of NO can lead to a  
29 decrease in sensitivity to the CIMS PAN measurements. For the conditions in Beijing, 10 ppbv of  
30 NO decreased the PAN sensitivity by 10% with higher levels decreasing the sensitivity further. NO  
31 levels above 10 ppbv were observed 20% of the time but only at night. Consequently, there is  
32 essentially no correction for the impact of NO during the day on PAN sensitivity. The measurement  
33 uncertainty of PAN at night during high levels of variable NO is larger than during the day.  
34 Detection limit for PAN is 7 pptv for 1 second integration period and a signal to noise ratio of 3.  
35 The uncertainties for PAN measurements are estimated to be 10%.

36 **HONO measurements.** HONO was measured with a liquid coil scrubbing/UV-vis  
37 instrument (*S5, S6*). Briefly, gaseous HONO was trapped quantitatively in a 10-turn coil sampler  
38 using 1mm phosphate buffer. The scrubbing solution was then derivatized with sulfanilamine  
39 (SA)/N-(1-naphthyl)-ethyldiamine (NED), subsequently analyzed using high-performance liquid  
40 chromatography (HPLC), and detected by UV-vis absorption.

41 Interferences during sampling were studied in our laboratory in Rome (*6*) and directly at  
42 Beijing using sodium carbonate denuders (*S7*). We used the denuder respectively in front of the  
43 Teflon tube and before the trap coils. The denuder in front of Teflon tube was used to study the  
44 possible formation of HONO from NO<sub>2</sub> and humidity on the tubing walls (*S8*). While, the denuder  
45 before the inlet traps was used to study the nitrite formation in the water solution due to: NO<sub>3</sub><sup>-</sup>  
46 +SO<sub>3</sub>→NO<sub>2</sub><sup>-</sup>+SO<sub>4</sub><sup>2-</sup>. Under summer conditions at Beijing we observed interferences on the order of

47 2–9% of the observed HONO mixing ratio. The inlet tube was 70 cm and the residence time of the  
48 air in the tube was less than 2 sec. The detection limit of the HONO instrument is less than 0.8 pptv.  
49 The uncertainty for HONO measurements is estimated to be 10%.

50 **VOC measurements.** C<sub>3</sub>-C<sub>9</sub> NMHCs were continuously measured with 30 minute time  
51 resolution, using a combination of two online GC-FID/PID systems (Syntech Spectra GC-FID/PID  
52 GC955 series 600/800 VOC analyzer) (S9), one for the C<sub>3</sub>-C<sub>5</sub> NMHCs, using a gas chromatograph  
53 with pre-concentration on Carbosieves SIII at 5 °C, followed by thermal desorption and separation  
54 on a capillary film column and a capillary PLOT column, and quantification by a photo ionization  
55 detector (PID) and a flame ionization detector (FID). The other system is for C<sub>6</sub>-C<sub>9</sub> NMHCs  
56 analysis; air samples are pre-concentrated on Tenax GR at normal temperature, thermal desorbed,  
57 separated on an ATTM-1 column, and detected by a PID. For each analysis, an air sample with a  
58 volume of 250mL was sampled. Calibration was performed before and after the campaign by using  
59 a gas standard containing 39 target species with mixing ratios of 1ppm in nitrogen, prepared by the  
60 gravimetric method (Spectra gases, Restek Corporation, USA). The detection limits are estimated to  
61 be 10 to 90 pptv, and the uncertainty is estimated to be 5%.

62 Another Automated GC/MS/FID system constructed of pre-concentrator with Varian 3800  
63 GC and Saturn 2200 MS was also deployed to measure VOCs. On each day two samples were  
64 collected and measured (8:00-9:00 and 13:00-14:00). To encompass VOCs of a wide range of  
65 volatility within each analysis, the system uses dual-columns and dual-detectors to simultaneously  
66 analyze both low and high-boiling compounds with each injection. The PLOT column connected to  
67 a FID was responsible for separation and detection of C<sub>2</sub>-C<sub>4</sub> compounds, and the DB-1 column  
68 was connected to the MS for separation and detection of MTBE and C<sub>4</sub>-C<sub>10</sub> compounds. Each  
69 aliquot of 190 ml from the canisters was drawn to the cryogenic trap packed with fine glass beads

70 cooled at  $-170\text{ }^{\circ}\text{C}$  for pre-concentration. During injection, the trap was resistively heated up to 80  
71  $^{\circ}\text{C}$  within seconds, and a stream of high purity He flushed the trapped VOCs onto the columns. The  
72 oven temperature was initially held at  $-50\text{ }^{\circ}\text{C}$  for 3.1 min, then ramped to  $-10\text{ }^{\circ}\text{C}$  at  $20\text{ }^{\circ}\text{C}/\text{min}$ , to  
73  $120\text{ }^{\circ}\text{C}$  at  $5\text{ }^{\circ}\text{C}/\text{min}$ , to  $180\text{ }^{\circ}\text{C}$  at  $20\text{ }^{\circ}\text{C}/\text{min}$ , and held at  $180\text{ }^{\circ}\text{C}$  for 21.5 min. The precision of the  
74 system was examined by repeatedly injecting a standard mixture made from Scott Marrin Company.  
75 In general, the precision for the C2–C10 NMHCs were usually below 3%. Linearity was tested by  
76 trapping a series of the same standard mixture of various concentrations (0.2-30ppbv). Most  
77 compounds exhibited good linearity with RSD of calibration response factors for measured species  
78 below than 10%.

79 OVOC compounds were measured using a newly developed PFPH-GC/MS method (*S10*).  
80 Three types of gaseous carbonyls, including formaldehyde, acetaldehyde and acetone were collected  
81 within 3-h sampling period onto an adsorbent (Tenax TA) coated with pentafluorophenyl hydrazine  
82 (PFPH) followed by thermal desorption and gas chromatographic (GC) analysis of the PFPH  
83 derivatives with mass spectrometric (MS) detection (Agilent, GC/MS, 6890/5973N). All of the  
84 tested carbonyls are shown to have method detection limits (MDLs) of sub-nanomoles per sampling  
85 tube, corresponding to air concentrations of  $< 0.3\text{ ppbv}$  for a sampled volume of 24 L. These limits  
86 are 2-12 times lower than those that can be obtained using the DNPH/HPLC method (*S10*). The  
87 uncertainty for OVOC measurements is estimated to be 10%.

88

## 89 **Additional descriptions of the 1-D REAM model**

90 **Oxidation mechanism of aromatics.** We adopt the aromatics-oxidation mechanism in the  
91 SAPRC-07 chemical mechanism developed for chemical transport models (*S14*). This mechanism is  
92 chosen because careful comparison between different mechanisms (e.g. SAPRC-99, 07, CB4,

93 RACM and the mechanism in REAM) indicates that SAPRC-07 mechanism is the most compatible  
94 with REAM and reflects the most recent updates of understanding of aromatics chemistry. In Table  
95 S1, we summarize the OH reactions for several key aromatic species, based on which the reactions  
96 for the lumped species (ARO1, ARO2) are derived. Among the products, only methylglyoxal  
97 (MGLY), glyoxal (GLYX), and biacetyl (BACL)) are shown because they are precursors for acetyl  
98 peroxy radical, which is of our interest in this work.

99 **Model VOC input.** Individual NMHC compounds were lumped into a number of model  
100 species to be used as model input. The mean concentrations for all the individual compounds and  
101 their corresponding lumped species are shown in Table S2. For species only measured at 8:00–9:00  
102 and 13:00–14:00, interpolations were conducted based on ratios between these compounds and  
103 other continuously measured compounds with similar lifetimes. Measured concentrations of  
104 acetone, acetaldehyde and formaldehyde were used in the model. Other OVOC species are  
105 simulated in the model.

106 **Estimation of Model errors.** The errors associated to the model are estimated as follows.  
107 The uncertainty associated with chemical mechanism is estimated to be less than 10% based on a  
108 sensitivity test, in which using different chemical mechanisms (RACM or REAM) only results in no  
109 more than 10% difference of simulated PAN. The uncertainty associated with transport is estimated  
110 to be 10% at most, because 5 times the modeled diffusion coefficient would only result in less than  
111 10% change of PAN at surface. Taking into account all these aspects, the total error in the model is  
112 estimated to be no more than 15% assuming transport and chemistry errors are not correlated and  
113 not accounting for the measurement uncertainties of precursors.

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116 **Literature Cited**

- 117 (S1) Ryerson, T. B.; Williams, E. J.; Fehsenfeld, F. C. An efficient photolysis system for fast-  
118 response NO<sub>2</sub> measurements. *J. Geophys. Res.-Atmos.*, **2000**, 105, 26447-26461.
- 119 (S2) Slusher, D. L.; Huey, L. G.; Tanner, D. J.; Flocke, F. M.; Roberts, J. M. A thermal dissociation-  
120 chemical ionization mass spectrometry (TD-CIMS) technique for the simultaneous  
121 measurement of peroxyacyl nitrates and dinitrogen pentoxide. *J. Geophys. Res.-Atmos.*, **2004**,  
122 *109*, D19315, doi:10.1029/2004JD004670.
- 123 (S3) Turnipseed, A. A.; Huey, L.G.; Nemitz, E.; Stickel, R.; Higgs, J.; Tanner, D.; Slusher, D.;  
124 Sparks, J.; Flocke F.; Guenther, A. Eddy Covariance Fluxes of Peroxyacetyl Nitrate (PAN) and  
125 NO<sub>y</sub> to a Coniferous Forest. *J. Geophys. Res.-Atmos.* **2006**, 111, D09304, doi:  
126 10.1029/2005JD006631.
- 127 (S4) Flocke, F. M.; Weinheimer, A. J.; Swanson, A. L.; Roberts, J. M.; Schmitt, R.; Shertz, S. On  
128 the measurement of PANs by gas chromatography and electron capture detection. *J. Atmos.*  
129 *Chem.*, **2005**, 52, 19-43.
- 130 (S5) Amoroso, A.; Beine, H. J.; Sparapani, R.; Nardino, M.; Allegrini, I. Observation of coinciding  
131 arctic boundary layer ozone depletion and snow surface emissions of nitrous acid. *Atmos.*  
132 *Environ.*, **2006**, 40, 1949-1956.
- 133 (S6) Amoroso, A.; Beine, H. J.; Esposito, G.; Perrino, C.; Catrambone, M.; Allegrini, I. Seasonal  
134 differences in atmospheric nitrous acid near Mediterranean urban areas. *Water Air Soil Pollut.*,  
135 **2008**, 188, 81-92.
- 136 (S7) Febo, A.; Perrino, C.; Cortiello M. A denuder technique for the measurement of nitrous acid in  
137 urban atmosphere. *Atmos. Environ.*, **1993**, 27A, 1721-1728.

- 138 (S8) Syomin, D. A.; Finlaysin-Pitt, B. J. HONO decomposition on borosilicate glass surfaces:  
139 implications for environmental chamber studies and field experiments. *Phy. Chem. Chem.*  
140 *Phys.*, **2003**, 5, 5236-5242.
- 141 (S9) Xie, X.; Shao, M.; Liu, Y.; Lu, S. H.; Chang, C. C.; Chen, Z. M. Estimate of initial isoprene  
142 contribution to ozone formation potential in Beijing, China. *Atmos. Environ.*, **2008**, 42, 6000-  
143 6010.
- 144 (S10) Ho, S. S. H.; Yu, J. Z. Determination of airborne carbonyls: Comparison of a thermal  
145 desorption/GC method with the standard DNPH/HPLC method. *Environ. Sci. Technol.*, **2004**,  
146 38, 862-870.
- 147 (S11) Zhao, C.; Wang, Y. H.; Zeng, T. East China Plains: A "Basin" of Ozone Pollution. *Environ.*  
148 *Sci. Technol.* **2009**, 43, 1911-1915.
- 149 (S12) Skamarock, W. C.; klemp, J. B.; Dudhia, J.; Gill, D. O.; Barker, D. M.; Wang, W.; Powers, J.  
150 G. A Description of the Advanced Research WRF Version 2. NCAR Tech. Note, June, **2005**.
- 151 (S13) Zhao, C.; Wang, Y. H.; Choi, Y.; Zeng T. Summertime impact of convective transport and  
152 lightning NO<sub>x</sub> production over North America: modeling dependence on meteorological  
153 simulations. *Atmos. Chem. Phys.*, **2009**, 9, 4315-4327.
- 154 (S14) Carter, W. P. L. Development of the SAPRC-07 chemical mechanism and updated ozone  
155 reactivity scales. Final Report to the California Air Resources Board Contract No. 03-318,  
156 **2009**.



157 **Tables and figures**158 **Table S1.** Reactions and rate constants for aromatics species with OH used in SAPRC-07 for deriving the lumped mechanism.

Species	Reactions	k	Mixing ratio (ppbv)	MGLY contribution (%)
Benzene	BENZENE + OH = 0.29 GLYX + Products	1.22E-12	2.2	1
Ethylbenzene	ETHYLBZ + OH = 0.184GLYX + 0.117MGLY + Products	7.00E-12	3.2	4
Toluene	TOLUENE + OH = 0.238 GLY + 0.151 MGLY + Products	5.58E-12	5.9	8
m-Xylene <sup>1</sup>	M-XYLENE + OH = 0.38 MGLY + Products	2.31E-11	2.2	31
o-Xylene	O-XYLENE + OH = 0.238 MGLY + 0.084GLYX + 0.185BACL + Products	1.36E-11	1.7	9
p-Xylene <sup>1</sup>	P-XYLENE + OH = 0.112 MGLY + 0.286GLYX + Products	1.43E-11	2.2	6
1,2,3-Trimethyl Benzene	123TMB + OH = 0.072 MGLY + 0.18GLYX + 0.447BACL+ Products	3.27E-11	0.3	1
1,2,4-Trimethyl Benzene	124TMB + OH = 0.405 MGLY + 0.074GLYX + 0.112BACL+ Products	3.25E-11	0.4	8
1,3,5-Trimethyl Benzene	135TMB + OH = 0.64 MGLY + Products	5.67E-11	0.5	32
ARO1 <sup>2</sup>	ARO1 + OH = 0.218 GLYX + 0.138 MGLY + Products	6.15E-12	11.3	15
ARO2 <sup>3</sup>	ARO2 + OH = 0.116 GLYX + 0.286 MGLY + 0.104 BACL + Products	2.57E-11	7.3	85

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160 <sup>1</sup> These two species were measured as one species mp-xylene, and we assume the same amount for each in this calculation.161 <sup>2</sup> ARO1 includes benzene (×30%), ethyl-benzene, and toluene.162 <sup>3</sup> ARO2 includes all aromatics other than those included in ARO1.

163 **Table S2.** Average mixing ratios (ppbv) of explicit and lumped NMHCs in the model.

<b>Alkanes</b>			<b>Alkenes</b>		
<b>C2H6<sup>1</sup></b>	Ethane <sup>2</sup>	3.82	<b>C2H4</b>	ethene	3.67
<b>C3H8</b>	<b>Propane<sup>3</sup></b>	<b>3.73</b>		<b>Propene</b>	<b>1.00</b>
	<b>isobutane</b>	<b>1.85</b>		<b>trans-2-butene</b>	<b>0.53</b>
	<b>n-butane</b>	<b>2.14</b>		<b>1-butene</b>	0.58
	<b>isopentane</b>	<b>3.50</b>		Isobutene	0.37
	<b>n-pentane</b>	<b>1.22</b>		<b>cis-2-butene</b>	<b>0.42</b>
	2,2-dimethylbutane	0.07		3-methyl-1-butene	0.08
	cyclopentane	0.14		<b>1,3-Butadiene</b>	<b>0.31</b>
	2-methylpentane	0.69		<b>1-pentene</b>	<b>0.57</b>
	3-methylpentane	0.50		<b>Isoprene</b>	<b>0.88</b>
	<b>n-hexane</b>	<b>1.40</b>	<b>PRPE</b>	<b>trans-2-pentene</b>	<b>0.24</b>
	2,4-dimethylpentane	0.06		cis-2-pentene	0.09
	methylcyclopentane	0.47		2-methyl-2-butene	0.18
<b>ALK4</b>	cyclohexane	0.18		Cyclopentene	0.03
	2-methylhexane	0.21		4-methyl-1-pentene	0.00
	2,3-dimethylpentane	0.09		2-methyl-1-pentene	0.08
	3-methylhexane	0.25		trans-2-hexene	0.00
	<b>2,2,4-trimethylpentane</b>	<b>0.47</b>		cis-2-hexene	0.04
	<b>n-heptane</b>	<b>3.47</b>		alpha-pinene	0.13
	methylcyclohexane	0.14			
	2,3,4-trimethylpentane	0.03		<b>Aromatics</b>	
	2-methylheptane	0.09		<b>Benzene</b>	<b>2.16</b>
	3-methylheptane	0.09	<b>ARO1</b>	<b>Toluene</b>	<b>5.88</b>
	<b>n-octane</b>	<b>0.91</b>		Styrene	0.12
	n-nonane	0.11		<b>Ethylbenzene</b>	<b>3.25</b>
	<b>Alkyne</b>			<b>m,p-xylene</b>	<b>4.30</b>
<b>C2H2</b>	ethyne	5.67		<b>o-xylene</b>	<b>1.68</b>
			<b>ARO2</b>	Isopropylbenzene	0.04
				n-propylbenzene	0.05
				<b>1,3,5-trimethylbenzene</b>	<b>0.54</b>
				<b>1,2,4-trimethylbenzene</b>	<b>0.37</b>
				<b>1,2,3-trimethylbenzene</b>	<b>0.32</b>

164  
165 <sup>1</sup> Model species are listed to the left and measured species are listed to the right. Lumped model  
166 species include multiple measured species.

167 <sup>2</sup>Species listed in normal font were measured at 8:00-9:00 and 13:00-14:00 each day; the averages  
168 of these measurements are shown.

169 <sup>3</sup>Species listed in bold font were measured continuously each hour; 24-hour averages are shown.

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