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Supplement of

**Peroxy radical measurements by ethane – nitric oxide
chemical amplification and laser-induced fluorescence
during the IRRONIC field campaign in a forest in Indiana**

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1 **S1. Calibration of NO₂ monitors**

2 Three cavity attenuated phase-shift spectrometry (CAPS) instruments (Aerodyne
3 Research) were used for measuring NO₂ (Kebabian et al., 2008;Kebabian et al., 2005). Two were
4 dedicated for the measurements of NO₂ as part of the ECHAMP measurement of peroxy radicals.
5 The third CAPS instrument was used for measuring ambient NO₂. The NO₂ monitors were
6 calibrated by sampling diluted NO₂(g) from a liquid permeation tube (Kin-Tek). The output of
7 the permeation tube (held at 40° C) was diluted into 100 sccm of N₂ and then into variable flow
8 rates (4000 to 8000 sccm) of either zero air or purified ambient air to make multiple points in the
9 calibration curve. The purified ambient air was prepared by passing ambient air through a
10 scrubber filled with sodium permanganate and activated charcoal (Purafil brand SP Blend
11 Media). The concentrations of NO₂ delivered from the permeation tube were quantified by a
12 chemiluminescence analyzer (Model 42i Trace Level, Thermo Scientific) where the NO₂ was
13 converted to NO (NO_x mode) in a molybdenum converter held at 325 °C. See section 3 below for
14 chemiluminescence sensor calibration information. The CAPS NO₂ measurements were also
15 checked by comparing the ECHAMP readings when in “Ox” (background) mode to
16 measurements of O₃ by a UV-absorption monitor (2B Tech model 202, accuracy 2%). The two
17 methods agreed to within 5% (Wood and Charest, 2014).

18 **S2. ECHAMP calibration**

19 The ECHAMP sensor was calibrated using the acetone photolysis method (Wood and Charest,
20 2014). Photolysis of acetone vapor produces almost equimolar concentrations of methyl peroxy
21 (CH₃O₂) and peroxyacetyl (CH₃C(O)OO) radicals:
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26 Following reaction with excess NO, these RO₂ radicals will produce NO₂ via the following
27 reactions:



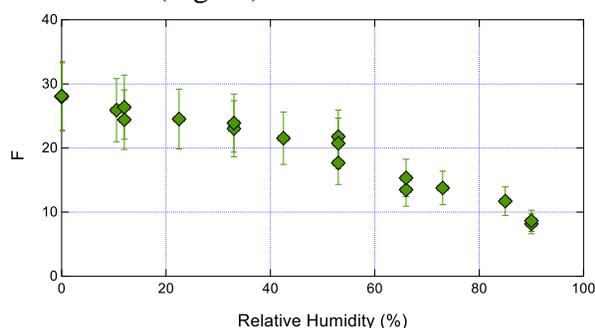
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36 Ignoring the formation of methyl nitrite (Reaction S5b), each CH₃O₂ radical would produce two
37 NO₂ molecules and each CH₃C(O)OO would produce three NO₂ molecules. The change in NO₂
38 observed when the radical source is modulated on and off, effected by diverting the acetone flow
39 away from the carrier flow that is illuminated by the UV source, is related to the RO₂ concentration
40 by the following equation:

$$41 \quad ([\text{CH}_3\text{O}_2] + [\text{CH}_3\text{C}(\text{O})\text{OO}]) = \Delta\text{NO}_2 / (2.44 \times 0.95) \quad (\text{S7})$$

42
43
44 in the absence of CH₃ONO formation and if acetone photolysis at 254 nm led to CH₃O₂ and
45 CH₃C(O)O₂ with unity photolysis quantum yield, then the denominator of the right-hand side of

46 the equation would be exactly 2.5. The two factors in the denominator account for these two
47 processes as described in Wood and Charest (2014).

48 As described in the main text, during the field July 2015 field deployment we produced
49 acetone vapor by flowing air over the headspace of dilute aqueous acetone rather than over pure
50 acetone. Unfortunately this produced variable amounts of blue light-absorbing compounds
51 (possibly glyoxal, methyl glyoxal, or diacetyl) which interfered with the CAPS detection of NO₂.
52 As a result we relied on laboratory calibrations performed in the laboratory rather than in-field
53 calibrations (Fig S1).



54
55 **Fig. S1.** Amplification factors obtained for ECHAMP using the acetone photolysis method.
56 Uncertainty bars reflect the 2 σ accuracy of 19%.

57
58

59 **S3. Sampling losses in the ECHAMP inlet.**

60 Sampled air flowed through a glass cross that is internally coated with halocarbon wax and
61 into the two FEP/PFA reaction chambers, both of which comprise a 1/4" PFA tee and 1/4" OD,
62 0.156" (0.4 cm) ID FEP tubing. The total residence time in the cross was approximately 18 ms.
63 We quantified potential sampling losses in the cross in two ways – 1. by quantifying the effective
64 first order wall loss rate constant of HO₂ and isoprene peroxy radicals onto halocarbon wax-coated
65 glass of the same dimensions, and 2. by comparing the ECHAMP signal when an HO₂ source was
66 used to overflow the sampling cross and comparing to the signal when the HO₂ source directly
67 overflowed one of the reaction chambers (at the PFA tee).

68 The wall loss rate constant measurements for several types of material will be fully
69 described in a separate manuscript. Briefly, peroxy radicals were produced by illumination of
70 humidified air (8 – 10 LPM) by UV radiation from a mercury lamp:

71



73

74 A 50 sccm flow of 0.1% CO was added to convert all OH into HO₂. Similarly, adding 50 sccm of
75 isoprene (40 ppm, balance N₂) to the flow converted all OH into isoprene peroxy radicals,

76 producing a mixture of 50% HO₂ and 50% isoprene peroxy radicals. This source was used to
77 overflow a quartz tube internally coated with halocarbon wax connected to the sampling cross, and
78 the transmitted radicals were quantified by ECHAMP. Four different lengths of tubing were used:
79 147 cm, 86", 25", and 0" (i.e., no tube).

80 The loss rate constants increased with RH, and at 60% RH were $1.6 \pm 0.6 \text{ s}^{-1}$ for HO₂ and
81 approximately 0.9 for HO₂/isopreneRO₂, indicating lower losses for isoprene RO₂ than for HO₂.
82 This suggests losses of HO₂ were only 3% during the 18 ms sampling time. Losses of CH₃O₂
83 radicals were similarly investigated and showed negligible losses (< 1%) onto halocarbon wax
84 and other fluoropolymers for sampling times under 1 second.

85 Similarly, the second method – comparing the ECHAMP signal when sampling a radical
86 source through the sampling cross or directly into one of the reaction chambers – indicated overall
87 losses of less than 4% for an HO₂ source.

88

89 **S4. Calibration of NO chemiluminescence monitor.**

90 The Thermo 42i-TL chemiluminescence monitor was calibrated by dilution of gas from a
91 30 ppm NO standard cylinder with zero grad air using MKS brand mass flow controllers (model
92 1179A). The flow rates from these flow controllers agreed to within 1% when measured by
93 separately calibrated flow meters (Definer 220, BIOS/Mesa Labs). The humidity dependence of
94 the chemiluminescence sensor was determined by humidification of the diluent zero air.

95

96 **S5. Baseline measurements for NO, NO₂, and O₃ measurements.**

97 Baseline (zero) measurements were executed every 10 minutes for the NO, NO₂, and O₃
98 measurements by overflowing their common inlet with purified air. This air was prepared by
99 drawing outdoor air sequentially through a PTFE filter, a diaphragm pump, 800 cm³ of KMnO₄(s),
100 600 cm³ of a blend of KMnO₄ and activated charcoal, and finally a second PTFE filter.

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103 **S6. Calculated Ozone Production Rates**

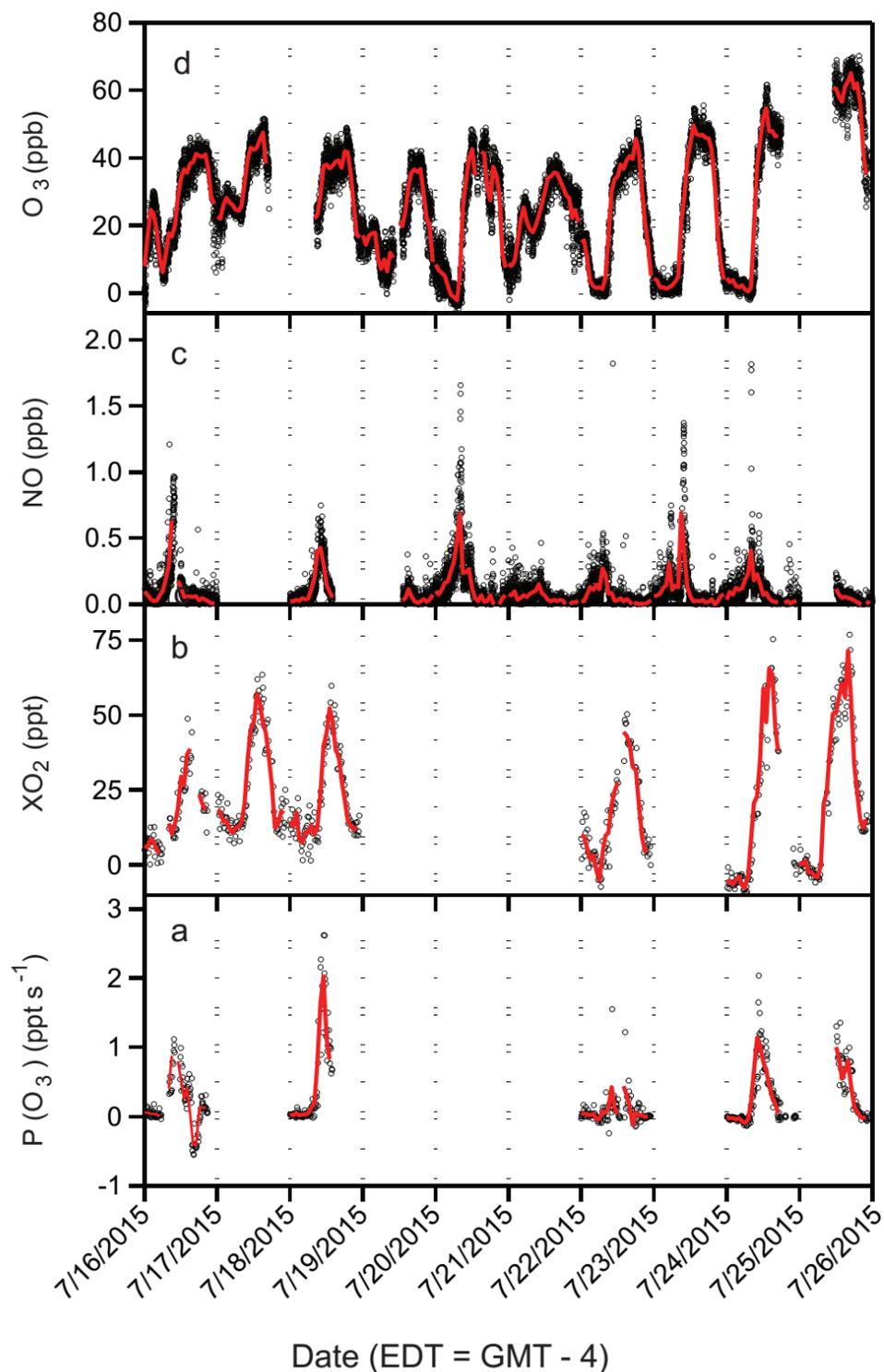
104 Net formation of ozone occurs when peroxy radicals oxidize NO to NO₂, followed by
105 photolysis of NO₂ (Seinfeld and Pandis, 2012; Finlayson-Pitts and Pitts Jr, 1999; Haagen-Smit et
106 al., 1954). Therefore, the instantaneous gross O₃ production rate (or more accurately, O_x
107 production rate where [O_x] ≡ [O₃] + [NO₂]) can be calculated by the following equation:
108

109
$$P(O_3) = k_{XO_2+NO}[XO_2][NO] \quad (S9)$$

110
111 where k_{XO_2+NO} is a weighted rate constant for the reaction of the various peroxy radicals with
112 NO. P(O₃) measurements are useful for assessing the temporal profile of ozone production, help
113 to quantify local production versus transport, and can identify the chemical regime (NO_x-limited
114 vs. NO_x-saturated) of an air mass. We use a value of $9 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ for the value of
115 k , reflecting a reasonable assumption that isoprene peroxy radicals and HO₂ had large
116 contributions to the total peroxy radical concentration. These two peroxy radicals react with NO
117 with rate constants of $9 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ and $8.8 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, respectively
118 (Atkinson et al., 2004; Sander et al., 2006). We note that the chemical amplification technique
119 does not detect the portion of organic peroxy radicals that form organic nitrates (RONO₂) upon
120 reaction with NO; thus no correction for organic nitrate yields are needed in equation 2.

121 P(O₃) values calculated based on 15-min average concentrations of the related chemical
122 species are shown in Fig. S1 along with XO₂ radicals, O₃ and NO during the IRRONIC campaign
123 over the time period of 16 July - 25 July. The missing P(O₃) data on Fig. 6 are due to unavailability
124 of either NO or XO₂ measurements due to calibrations or technical problems with the
125 chemiluminescence instrument. 15-min average P(O₃) values between 9:00 and 21:00 were at most
126 9.4 ppb hr⁻¹, with significant inter-day variability. For example P(O₃) exceeded 7.0 ppb/hr for
127 several hours on 18 July but never exceeded 5.0 ppb/hr on 22 or 16 July. Peak P(O₃) values
128 occurred between 9 and 11 am, with average values between 3.3 and 7.8 ppb hr⁻¹.

129



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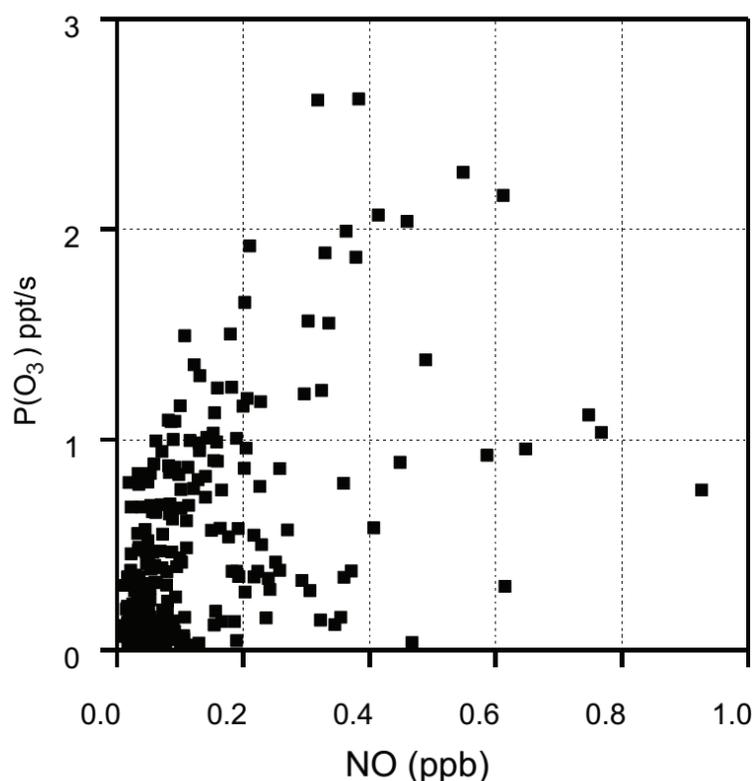
131 **Fig S2.** Temporal variations of a) calculated ozone production rate ($P(O_3)$), b) total peroxy
 132 radicals (XO_2), c) NO and d) O_3 during the IRRONIC campaign over the time period of 16 July
 133 to 25 July. The missing values of $P(O_3)$ are related with the unavailability of either XO_2 or NO
 134 measurements.

135 The observed $P(O_3)$ values at our study site are in general lower than those observed in urban
136 areas, which have exceeded 50 ppb h^{-1} in Mexico City and Houston (Cazorla et al.,
137 2012; Kleinman et al., 2005; Shirley et al., 2006). The main reason is that both the NO
138 concentrations and primary HOx production rates (from $O(^1D) + H_2O$ and the photolysis of
139 HONO and oxygenated VOCs) were significantly lower during the IRRONIC campaign
140 compared to those reported in the mentioned urban areas. $P(O_3)$ was highest in the late morning
141 (9 – 11 am) when NO was highest as well. The overall positive correlation between $P(O_3)$ and
142 [NO] suggests that ozone production regime was almost always NO_x -limited (see Fig. S2).

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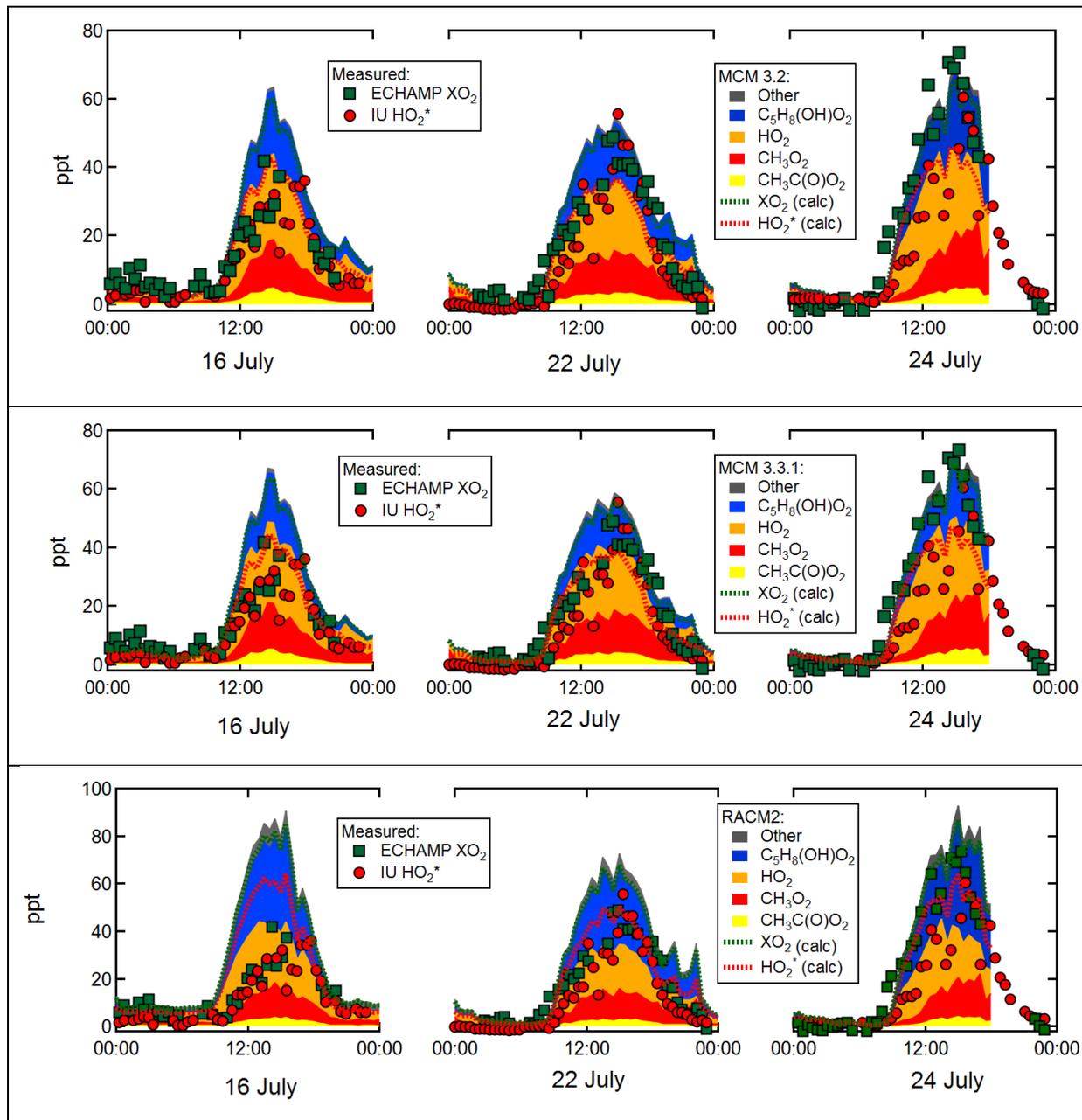
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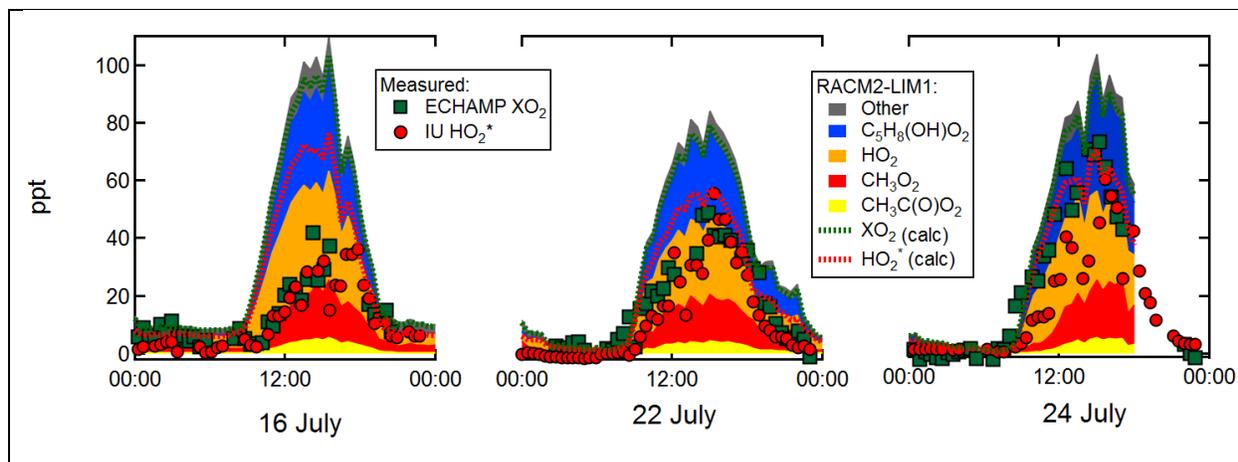
149 **Fig. S3.** Relationship between $P(O_3)$ and NO during the daytime (09:00 to 21:00) over the time
150 period of 13-25 July.

151

152 **S6. Comparison of Peroxy radical speciation predicted by RACM2, RACM2-LIM1, MCM**
 153 **3.2, and MCM 3.3.1**

154
 155 The four figures below show the modeled composition of peroxy radicals predicted by the four
 156 chemical mechanisms.
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Fig S4. Peroxy radical concentrations predicted by the four chemical mechanisms

162
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Table S1. Summary of modeled and measured concentrations and ratios between 13:00 and 18:00.

	16 Jul	22 Jul	24 Jul
Measured	28.4	38.9	58.6
[XO ₂]			
[HO ₂ *]	26.9	34.5	41.5
[XO ₂]/[HO ₂ *]	1.06	1.13	1.41
MCM32	38.1	44.1	55.2
[XO ₂]			
[HO ₂ *]	29.8	31.4	38.3
[XO ₂]/[HO ₂ *]	1.39	1.41	1.45
MCM331	49.8	47.5	57.2
[XO ₂]			
[HO ₂ *]	35.2	32.8	38.9
[XO ₂]/[HO ₂ *]	1.42	1.46	1.48
RACM2	66.1	56.7	69.4
[XO ₂]			
[HO ₂ *]	50.3	42.4	51.1
[XO ₂]/[HO ₂ *]	1.32	1.34	1.36
RACM2-LIM1	81.3	67.4	79.2
[XO ₂]			
[HO ₂ *]	60.3	49.3	57.5
[XO ₂]/[HO ₂ *]	1.35	1.37	1.38

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