

1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30

Supplementary Material

Comparison of the Chemical Evolution and Characteristics of 495 Biomass Burning Plumes Intercepted by the NASA DC-8 Aircraft during the ARCTAS/CARB-2008 Field Campaign

A. Hecobian¹, Z. Liu¹, C.J. Hennigan^{1#}, L. G. Huey¹, J.L. Jimenez², M.J. Cubison², S. Vay³, G. Diskin³, G. Sachse³, A. Wisthaler⁴, T. Mikoviny⁴, A. Weinheimer⁵, D. Knapp⁵, P.O. Wennberg⁶, A. Kürten⁷, J.D. Crouse⁶, J. St Clair⁶, Y. Wang¹, W.H. Brune⁸ and R.J. Weber¹

[1]{School of Earth and Atmospheric Sciences, Georgia Institute of Technology, Atlanta, GA, USA }

[2]{Department of Chemistry and Biochemistry and Cooperative Institute for Research in Environmental Sciences (CIRES), University of Colorado, Boulder, CO, USA }

[3]{NASA/Langley Research Center, Hampton, VA, USA }

[4]{Institute for Ion Physics and Applied Physics, Innsbruck University, Innsbruck, Austria }

[5]{National Center for Atmospheric Research, Boulder, CO, USA }

[6]{Atmospheric Chemistry and Environmental Engineering, California Institute of Technology, Pasadena, CA, USA }

[7]{Institute for Atmospheric and Environmental Sciences, Johann Wolfgang Goethe University Frankfurt am Main, 60438 Frankfurt am Main, Germany }

[8]{Department of Meteorology, Pennsylvania State University, University Park, PA, USA }

[#]{Now at Center for Atmospheric Particle Studies, Carnegie Mellon University, Pittsburgh, Pennsylvania, USA }

Correspondence to: Arsineh Hecobian (arsineh@gatech.edu); Rodney Weber (rodney.weber@eas.gatech.edu)

31 To further investigate the oxidation environment in the boreal fire plumes, we ran
32 a box model simulation for the 1 July 2008 fire plume. This specific plume was chosen
33 as it has more data, over the observed time range, than the others. The box model was
34 based on a 3-D photochemical transport model (REAM) (Choi et al., 2008; Zhao et al.,
35 2009) with updated VOC chemistry by (Carter, 2009). Measured photolysis reaction
36 rates (J-values) were used whenever possible; other photolysis reaction rates were scaled
37 by the ratio of observed to simulated J values of NO₂. Observations of O₃, PANs, CO,
38 VOCs, NO, NO₂, OH, HO₂, H₂O₂, alcohols and organic acids, as well as meteorological
39 parameters such as water vapor and temperature, were used to constrain the model with a
40 5-minute time step. The time evolution of chemical species of interest was simulated.
41 Dilution was not considered.

42 Two sets of model runs were conducted. We first constrained the model with all
43 available measurements to determine the chemical production and loss rates for O_x (O_x =
44 O₃ + NO₂ + NO₃ + PAN + PPN + PMN + HNO₄ + N₂O₅ + HNO₃). In the second set, we
45 simulated O₃ and PAN concentrations to compare with the observed values.

46

47 **1 Model results**

48 Production and loss rates of O₃ and PAN are diagnosed from the fully constrained
49 model run and shown in Figs. 1S and 2S, respectively. The lifetime of PAN, which is a
50 function of temperature, is also shown. We show the comparisons of observed and
51 simulated O₃ and PAN in Figs. 3S and 4S, respectively.

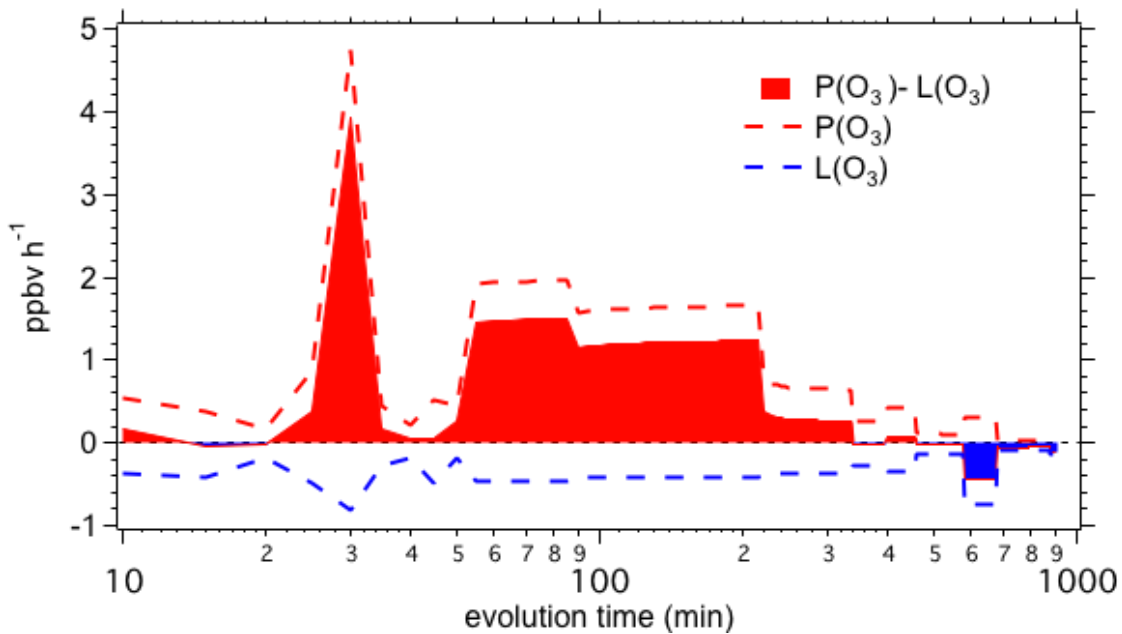
52 The model simulates a net O₃ production in the first 3 hours. The rate of ~ 1
53 ppbv/hr gives an increase of ~ 3 ppbv over this period, which is relatively small
54 compared to the O₃ mixing ratio of > 30 ppbv. During this period, NO_x mixing ratio

55 drops from > 500 pptv to < 100 pptv. Simulated HO₂ is in the range of 10-25 pptv in
56 agreement with the observations (Fig. 5S), simulated OH is in the range of 2 – 6 x 10⁶
57 molecules cm⁻³.

58 The simulated lifetime of PAN is several hours because of relatively high
59 temperature in the boundary layer. At the later stage, the plume rises to an altitude of 5
60 km and the lifetime of PAN is much longer because of lower temperatures. Initially NO_x
61 is converted to PAN in the plume at a rate of ~80 pptv/h in the first 3 hours. Relative to
62 the average PAN mixing ratio of 400 pptv, this production is significant. As the plume
63 ages and NO_x mixing ratio decreases to ~50 pptv, PAN is lost, providing a NO_x source.

64 Simulated O₃ mixing ratio in the plume increases slightly. The relative increase is
65 larger for simulated PAN in the first 3 hours. The observed variation of PAN (relative to
66 mean values) is much larger than that of O₃. The model fails to capture the observed
67 variation. The heterogeneity of PAN observations in the fresh plume may reflect in part
68 the large variations of NO_x or VOCs emissions in the fire.

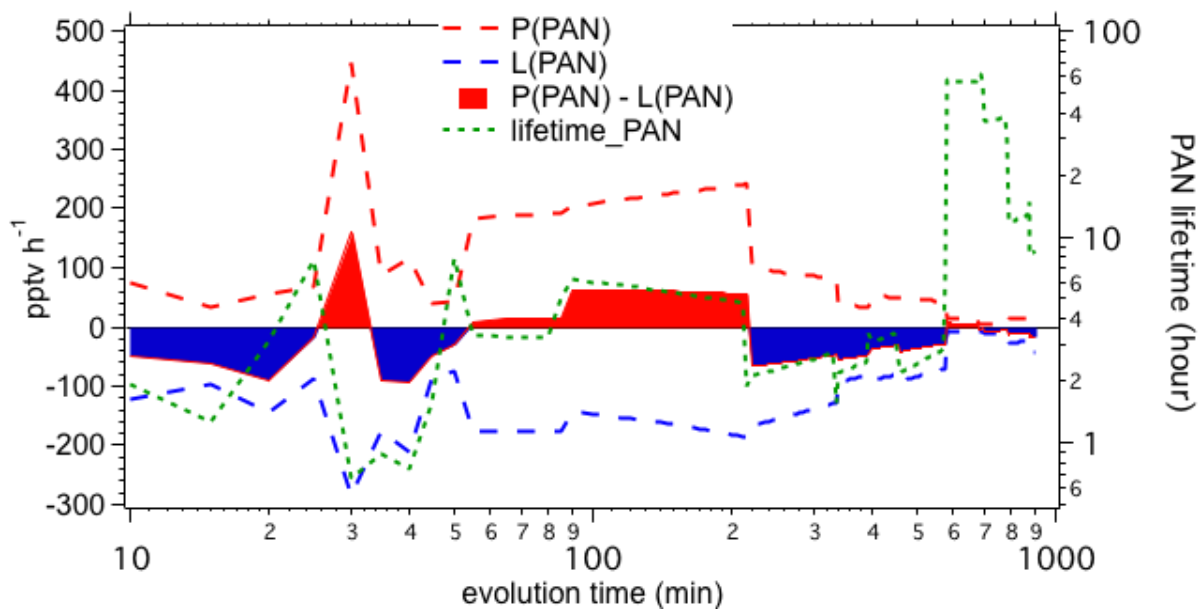
69



70

71 **Figure 1S.** Simulated O₃ production and loss rates and net formation rate as a function of
 72 time.

73



74

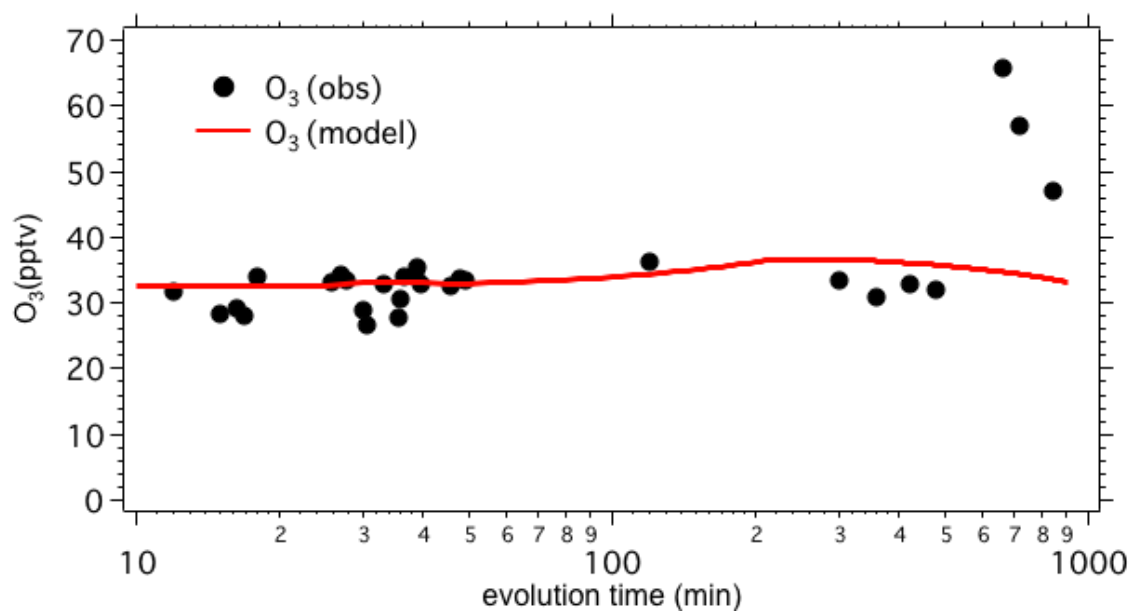
75

76 **Figure 2S.** Simulated PAN production and loss rates and net formation rate. The
 77 estimated lifetime of PAN is also shown.

78

79

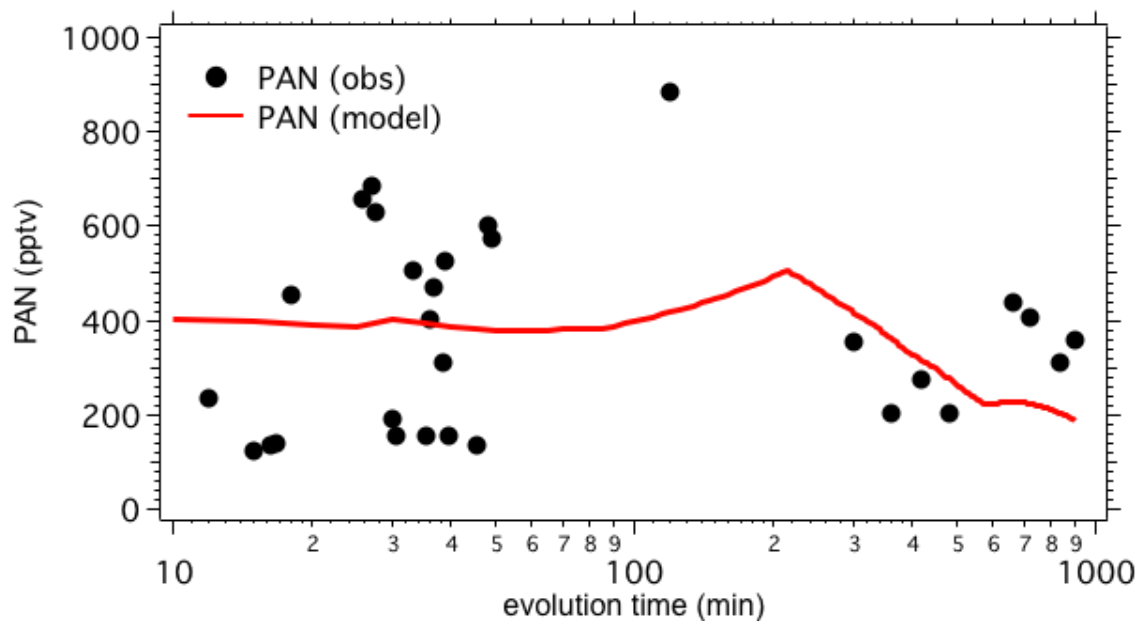
80



81

82 **Figure 3S.** Simulated and observed O₃ concentrations as a function of time.

83



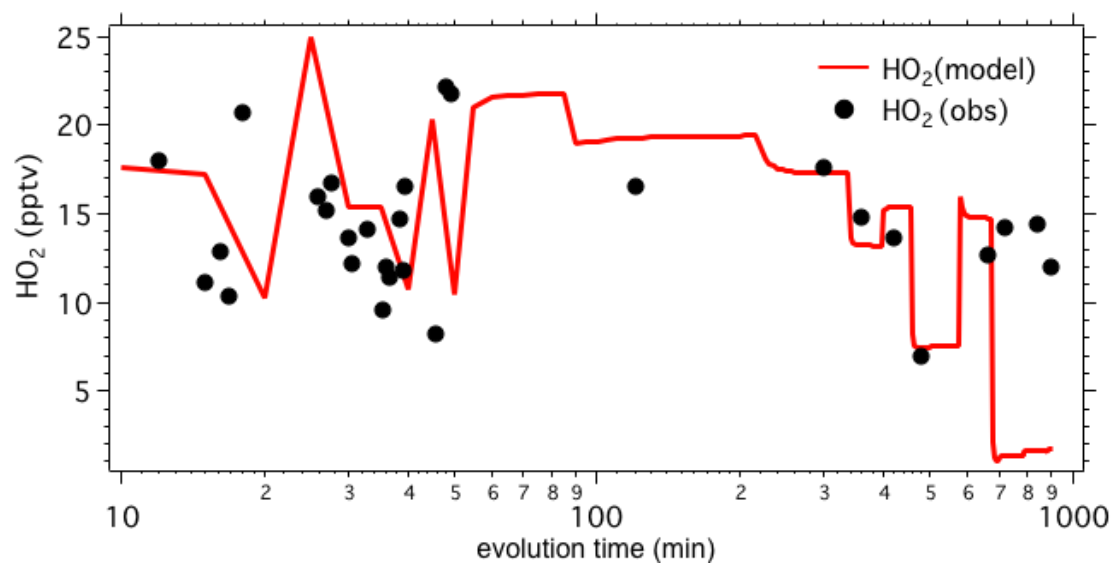
84

85 **Figure 4S.** Simulated and observed PAN concentrations as a function of time.

86

87

88



89

90 **Figure 5S.** Simulated and observed HO₂ concentrations as a function of time.