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

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To further investigate the oxidation environment in the boreal fire plumes, we ran a box model simulation for the 1 July 2008 fire plume. This specific plume was chosen as it has more data, over the observed time range, than the others. The box model was based on a 3-D photochemical transport model (REAM) (Choi et al., 2008; Zhao et al., 2009) with updated VOC chemistry by (Carter, 2009). Measured photolysis reaction rates (J-values) were used whenever possible; other photolysis reaction rates were scaled by the ratio of observed to simulated J values of NO_2. Observations of O_3, PANs, CO, VOCs, NO, NO_2, OH, HO_2, H_2O_2, alcohols and organic acids, as well as meteorological parameters such as water vapor and temperature, were used to constrain the model with a 5-minute time step. The time evolution of chemical species of interest was simulated. Dilution was not considered.

Two sets of model runs were conducted. We first constrained the model with all available measurements to determine the chemical production and loss rates for O_x (O_x = $O_3 + NO_2 + NO_3 + PAN + PPN + PMN + HNO_4 + N_2O_5 + HNO_3$). In the second set, we simulated O_3 and PAN concentrations to compare with the observed values.

1 Model results

Production and loss rates of O_3 and PAN are diagnosed from the fully constrained model run and shown in Figs. 1S and 2S, respectively. The lifetime of PAN, which is a function of temperature, is also shown. We show the comparisons of observed and simulated O_3 and PAN in Figs. 3S and 4S, respectively.

The model simulates a net O_3 production in the first 3 hours. The rate of ~ 1 ppbv/hr gives an increase of ~ 3 ppbv over this period, which is relatively small compared to the O_3 mixing ratio of > 30 ppbv. During this period, NO_x mixing ratio

drops from > 500 pptv to < 100 pptv. Simulated HO_2 is in the range of 10-25 pptv in agreement with the observations (Fig. 5S), simulated OH is in the range of 2 – 6 x 10^6 molecules cm^{-3}.

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

Simulated O_3 mixing ratio in the plume increases slightly. The relative increase is larger for simulated PAN in the first 3 hours. The observed variation of PAN (relative to mean values) is much larger than that of O_3. The model fails to capture the observed variation. The heterogeneity of PAN observations in the fresh plume may reflect in part the large variations of NO_x or VOCs emissions in the fire.

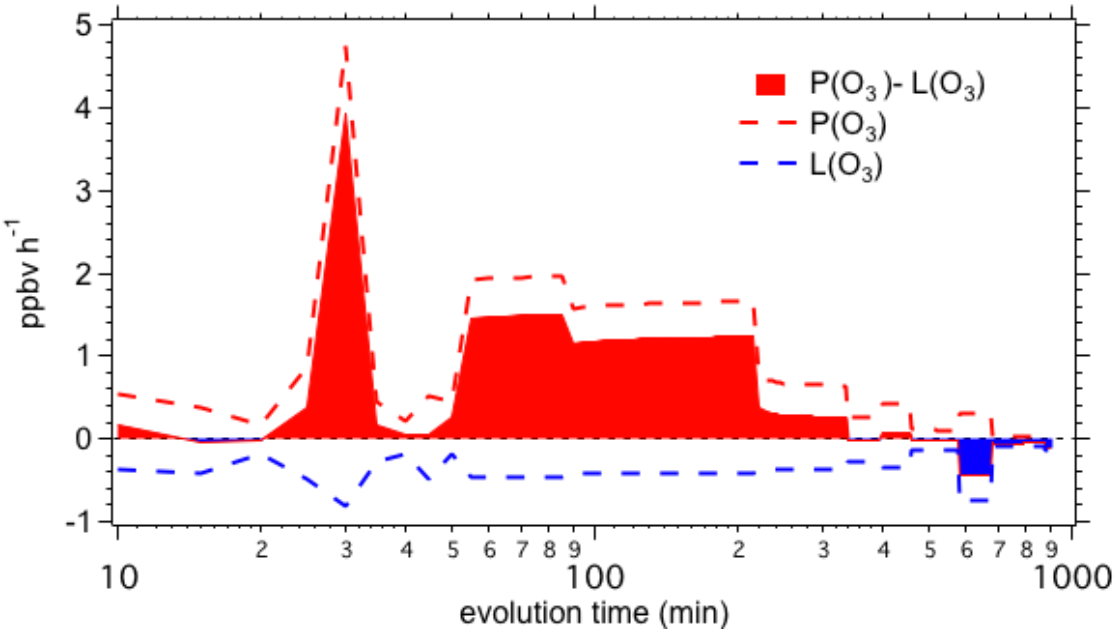

Figure 1S. Simulated O_3 production and loss rates and net formation rate as a function of time.

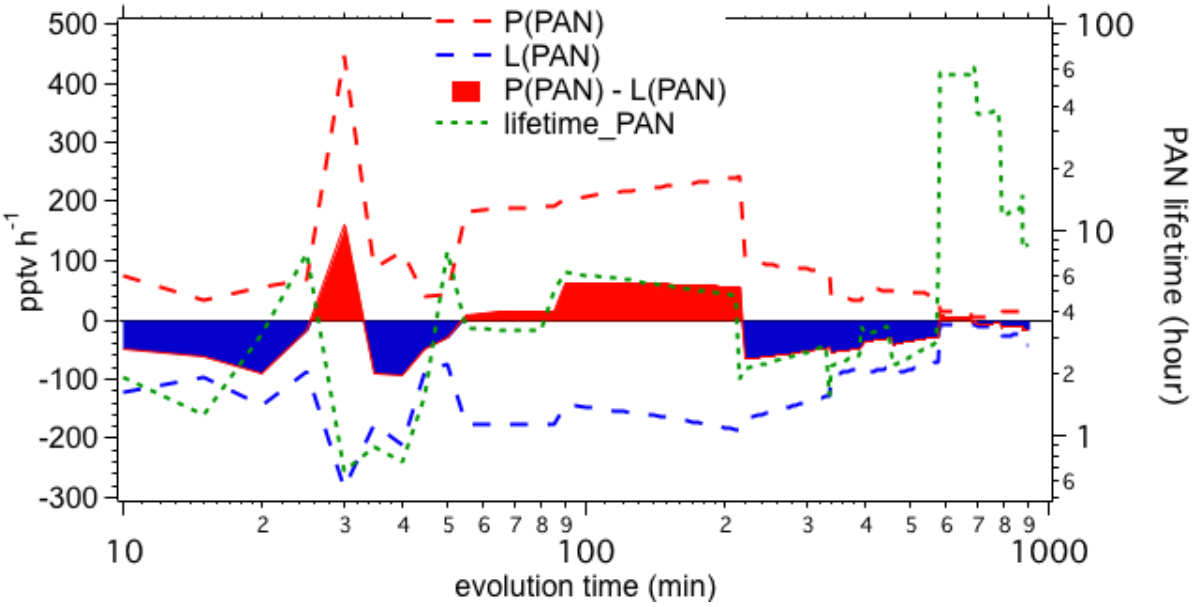

Figure 2S. Simulated PAN production and loss rates and net formation rate. The estimated lifetime of PAN is also shown.

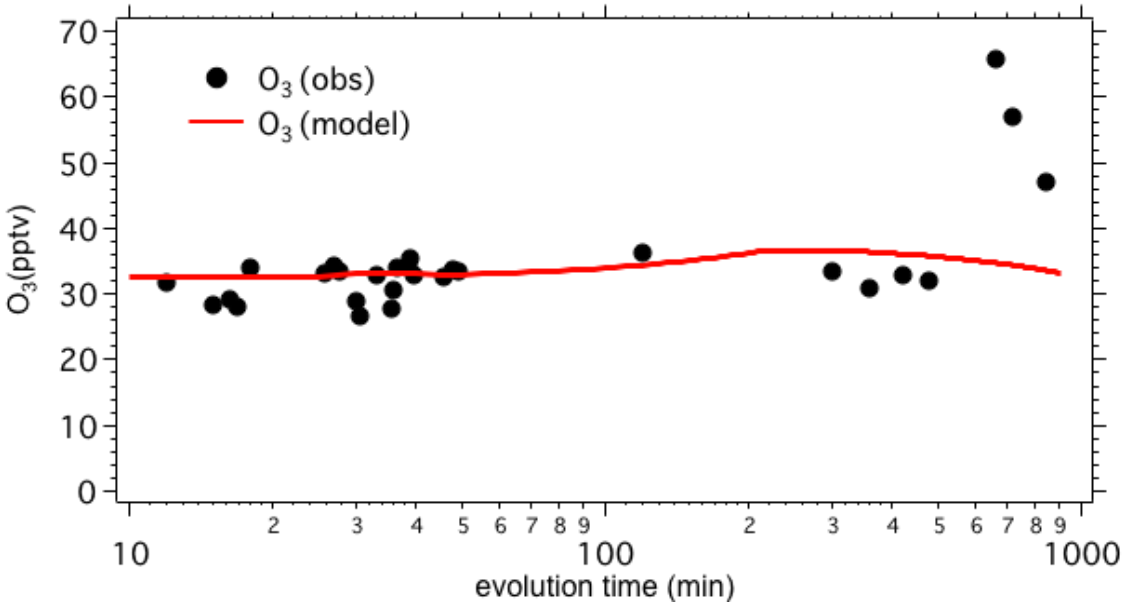

Figure 3S. Simulated and observed O_3 concentrations as a function of time.

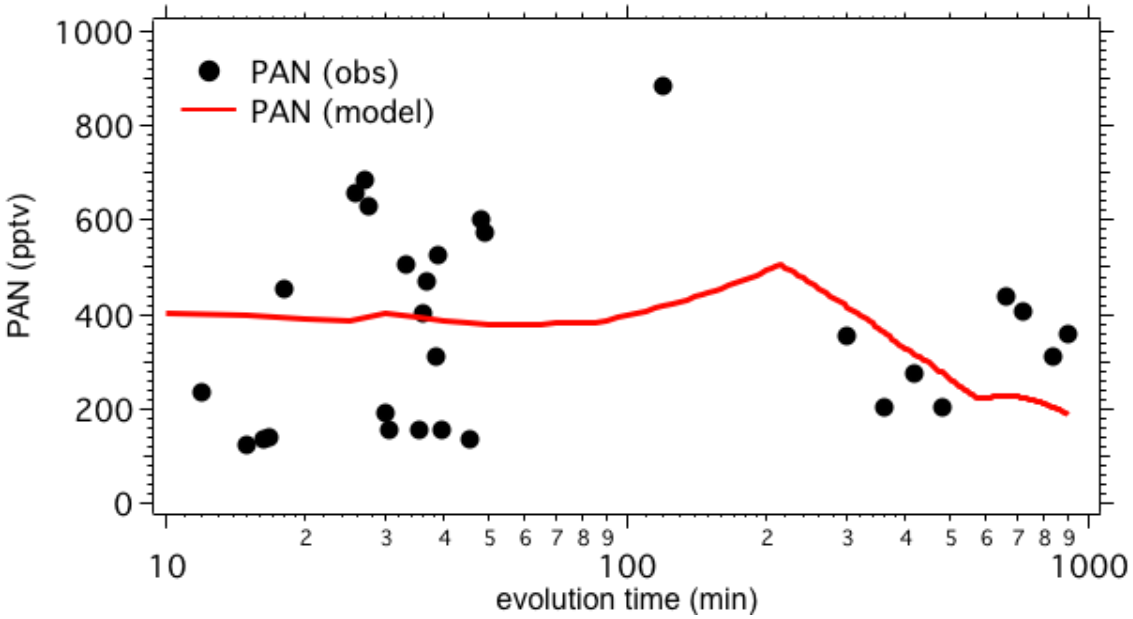

Figure 4S. Simulated and observed PAN concentrations as a function of time.

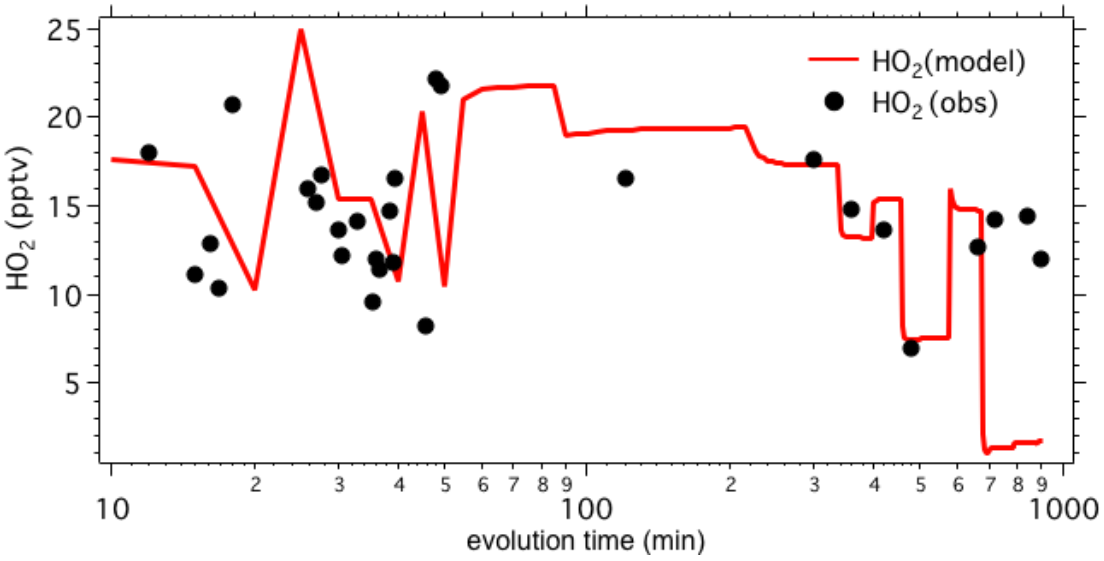

Figure 5S. Simulated and observed HO_2 concentrations as a function of time.