

SUPPORTING ONLINE MATERIAL

CMAQ Modeling Methods

The Community Multiscale Air Quality (CMAQ) model is a comprehensive urban to inter-continental scale atmospheric chemistry/transport/deposition modeling system that is being widely used for research, regulation and forecasting applications. Version 4.6 of CMAQ includes biogenic SOA from terpenes and anthropogenic SOA from aromatic compounds. The aerosol distribution is modeled as a superposition of three lognormal modes that corresponds to the Aitken, accumulation and coarse modes. A more complete description is given by Yu et al. (2007) (1). CMAQ was applied to a geographic domain encompassing the eastern U.S. The horizontal domain was discretized using a grid of 12 km resolution, while the vertical extent ranging from the surface to 100 mb was discretized with fourteen layers of variable thickness.

The meteorology for these CMAQ simulations was developed using the MM5 v3.6.3 model (2). Specific options used for these MM5 simulations include the Pleim-Xiu land surface scheme, Reisner 2 microphysics, Kain-Fritsch cumulus parameterization, and RRTM radiation parameterization. The MM5 analysis nudging option was exercised to assimilate observations into the simulation, and the MM5 simulation was reinitialized every four days. To create model-ready meteorology inputs for CMAQ, the MM5 results were then processed using the Meteorology-Chemistry Interface Program (MCIP) version 3.

To estimate the criteria pollutant emissions for 2004 simulated by CMAQ, the USEPA National Emission Inventory 2001 was updated for the time period of interest

(<http://www.epa.gov/ttn/chief/net/critsummary.html>). The base 2001 inventories for summer 2004 were updated with point source emissions from CEM observational data and the Mobile 6 emission model (<http://www.epa.gov/otaq/m6.htm>). By re-running Mobile6, the emissions corresponded with the correct motor fleet and meteorology for that time period. Biogenic emissions were estimated based on the meteorological predictions for summer 2004 using BEIS 3.13 (www.cmascenter.org).

SOA yield parameterization

A new model species (AORGC) was created in CMAQ to represent cloud-produced SOA. Two yield-based chemical reactions (glyoxal + $\cdot\text{OH}$ and methylglyoxal + $\cdot\text{OH}$) were added to the CMAQ aqueous chemistry module (*aqchem*) to produce the new aerosol species. The SOA yields used in these simulations were 1% (lower bound), 10% (higher bound) and 4%. Organic material reacted in the aqueous phase and not retained as aerosol (e.g., 96% of reacted glyoxal and methylglyoxal) was assumed to form CO_2 (Figure S-5) and the applied yield values account for this carbon loss.

Maximum SOA yields are typically employed in atmospheric modeling. The maximum mass-based yields for species likely to contribute to SOA during glyoxal experiments are reported to be 2% (for oxalic acid) and 30% (for higher molecular weight species) (3). However, these yields were calculated at reaction times unrealistic for cloud processing. For example, in one pass of an air parcel through a cloud, the typical cloud contact time is on the order of 10 minutes (4). A mass based yield for oxalic acid at 10 minutes is reported to be 1% (3). The 10 minute mass yield for higher molecular weight species, calculated for this work from total organic carbon measurements, was 9%.

Specifically, at ~ 10 minutes during glyoxal experiments, quantified carboxylic acids (i.e., oxalic, glyoxylic and formic acids) accounted for 98% of measured carbon. We assume that 2% of the carbon at 10 minutes is higher molecular weight species, with average characteristics of 177 g mole^{-1} and an organic mass to organic carbon ratio (OM:OC) of 2 (5).

Species concentrations in the aqueous chemistry module (*aqchem*) of CMAQ are calculated in molar units (moles L^{-1}) and therefore yield values were converted to a molar basis prior to stoichiometric application in CMAQ. Oxalic acid and higher molecular weight species are both expected to contribute to SOA and in this simulation their molar yields (~1% and 3% respectively) are added together for the applied “AORGC” 4% molar yield. AORGC in CMAQ employs the higher molecular weight species characteristics (e.g., molecular weight and OM:OC ratio). We point out that using these average values does not artificially create organic carbon or mass in the aqueous phase. For example, the 0.04 molar yield of organic mass per mole of reacted aldehyde corresponds to 0.3 moles of carbon in the aerosol species per 2 moles of carbon in a reacted mole of glyoxal, or 3 moles of carbon in a reacted mole of methylglyoxal. There is a net carbon loss to CO_2 and this indicates that CMAQ will not artificially create organic mass or carbon through the introduction of this process.

A new generalized Rosenbrock solver for a more explicit treatment of the aqueous chemistry appropriate for inclusion in CMAQ is currently being developed. The current aqueous chemistry solver (forward Euler method for oxidation calculations and bisection for pH calculation) is not suitable for a more complex treatment of this SOA formation

process. The investment in a new solver is warranted by our findings that suggest the cloud-production of SOA is significant. The new aqueous solver will allow for and include photolysis reactions and explicit treatment of the chemistry.

Hydroxyl Radical Concentration

Model results likely represent lower boundaries for aqueous $\cdot\text{OH}$ concentrations because only gas phase $\cdot\text{OH}$ production followed by gas-to-aqueous partitioning (according to Henry's Law) was considered, though the neglected aqueous production reactions (e.g., direct photolysis of H_2O_2 and NO_3^-) are thought to be minor (6). A lower initial $\cdot\text{OH}$ concentration (due to partitioning only) likely creates a lower bound for cloud-produced SOA concentrations. Detailed off-line box modeling using typical initial aqueous concentrations observed in the 3-dimensional CMAQ simulation indicates that SOA_{cld} is sensitive to the initial $\cdot\text{OH}$ concentration, i.e., a lower initial $\cdot\text{OH}$ concentration resulted in a lower resulting AORGC concentration, suggesting these results are conservative. While we think $\cdot\text{OH}$ aqueous phase concentrations are low, we point out that we can not be certain because aqueous phase (cloud) measurements of $\cdot\text{OH}$ and CMAQ's ability to predict $\cdot\text{OH}$ in the aqueous phase remains to be investigated.

Model Results

Note that cloud cover in the eastern U.S. was widespread on August 14 and in general the model can predict such conditions well (Figure S-4). On days when cloud fields were not predicted well, and when the aircraft was specifically flying in and out of urban and power plant plumes OC/WSOC time series comparisons were not as

successful, though model performance did improve as indicated by a reduction in normalized mean bias and increases in correlation for each compared flight (Table S-1).

References

1. Yu, S.; Bhawe, P. V.; Dennis, R. L.; Mathur, R., Seasonal and regional variations of primary and secondary organic aerosols over the Continental United States: Semi-empirical estimates and model evaluation. *Environ. Sci. Technol.* **2007**, *41*, (13), 4690-4697.
2. Grell, G. A.; Dudhia, J.; Stauffer, D. R. *A description of the fifth-generation Penn State-NCAR Mesoscale Model (MM5)*; NCAR Tech. Note NCAR/TN-398+STR; National Center for Atmospheric Research: Boulder, CO, 1994; p 122.
3. Carlton, A. G.; Turpin, B. J.; Altieri, K. E.; Reff, A.; Seitzinger, S.; Lim, H. J.; Ervens, B., Atmospheric Oxalic Acid and SOA Production from Glyoxal: Results of Aqueous Photooxidation Experiments. *Atmos. Environ.* **2007**, *41*, (35), 7588-7602.
4. Ervens, B.; Feingold, G.; Frost, G. J.; Kreidenweis, S. M., A modeling study of aqueous production of dicarboxylic acids: 1. Chemical pathways and speciated organic mass production. *J. Geophys. Res.* **2004**, *109*, (D15205), doi:10.1029/2003JD004387.
5. Altieri, K. E.; Seitzinger, S. P.; Carlton, A. G.; Turpin, B. J.; Klein, G. C.; Marshall, A. G., Oligomers formed through in-cloud methylglyoxal reactions: chemical composition, properties, and mechanisms investigated by ultra-high resolution FT-ICR mass spectrometry. *Atmos. Environ.* **2008**, *42*, 1476-1490 doi:10.1016/j.atmosenv.2007.11.015.
6. Arakaki, T.; Faust, B. C., Sources, sinks, and mechanisms of hydroxyl radical ((•OH)-O-center dot) photoproduction and consumption in authentic acidic continental cloud waters from Whiteface Mountain, New York: The role of the Fe(r) (r=II, III) photochemical cycle. *J. Geophys. Res.-Atmos.* **1998**, *103*, (D3), 3487-3504.
7. Sullivan, A. P.; Peltier, R. E.; Brock, C. A.; de Gouw, J. A.; Holloway, J. S.; Warneke, C.; Wollny, A. G.; Weber, R. J., Airborne measurements of carbonaceous aerosol soluble in water over northeastern United States: Method development and an investigation into water-soluble organic carbon sources. *J. Geophys. Res.-Atmos.* **2006**, *111*, (D23).

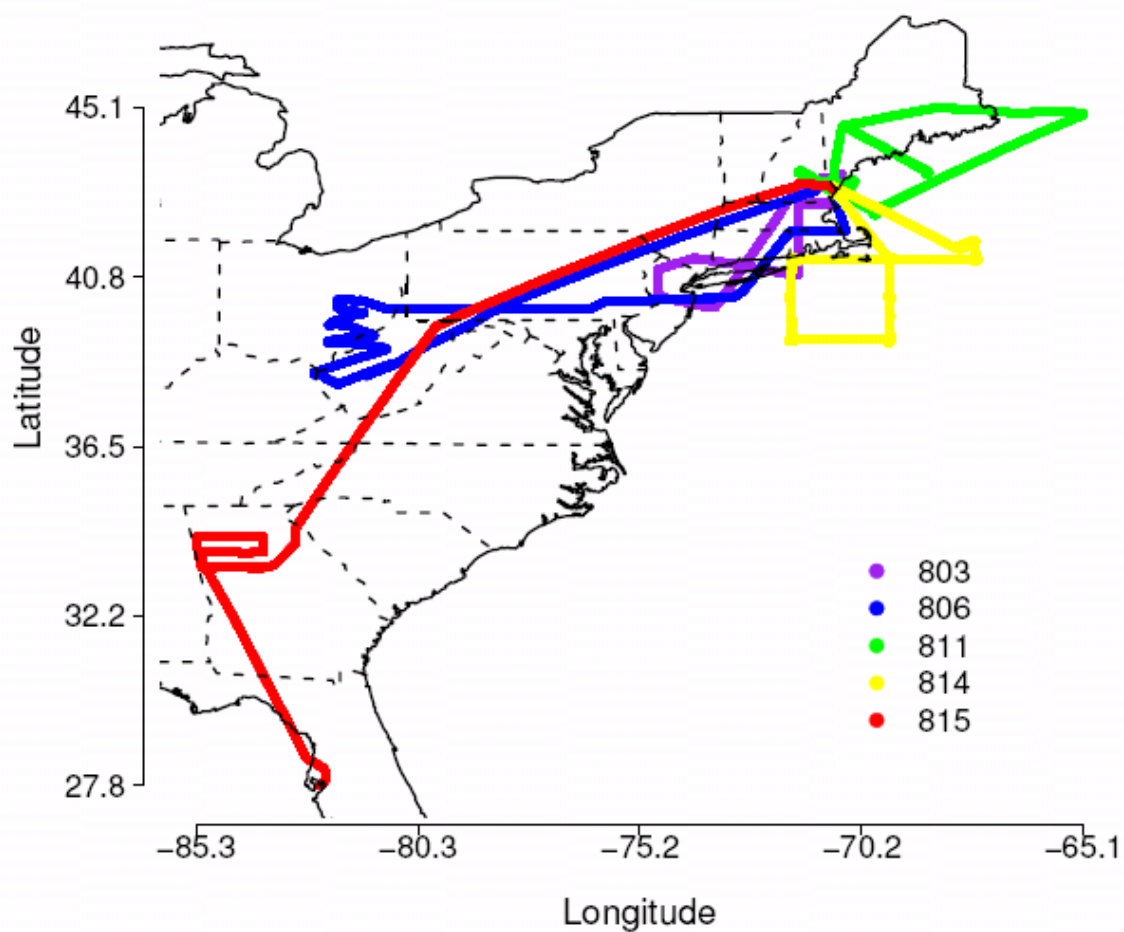


Figure S-1. NOAA-P3 Flight Trajectories for Compared Flights

Aug. 3rd (803) flight – New England at dawn; Aug. 6th (806) flight – Ohio Valley power plant plumes; Aug. 11th (811) flight – New York City urban plume at night; Aug. 14th (814) flight – widespread clouds; Aug. 15th (815) flight – transit to Florida with sampling of Atlanta urban plume

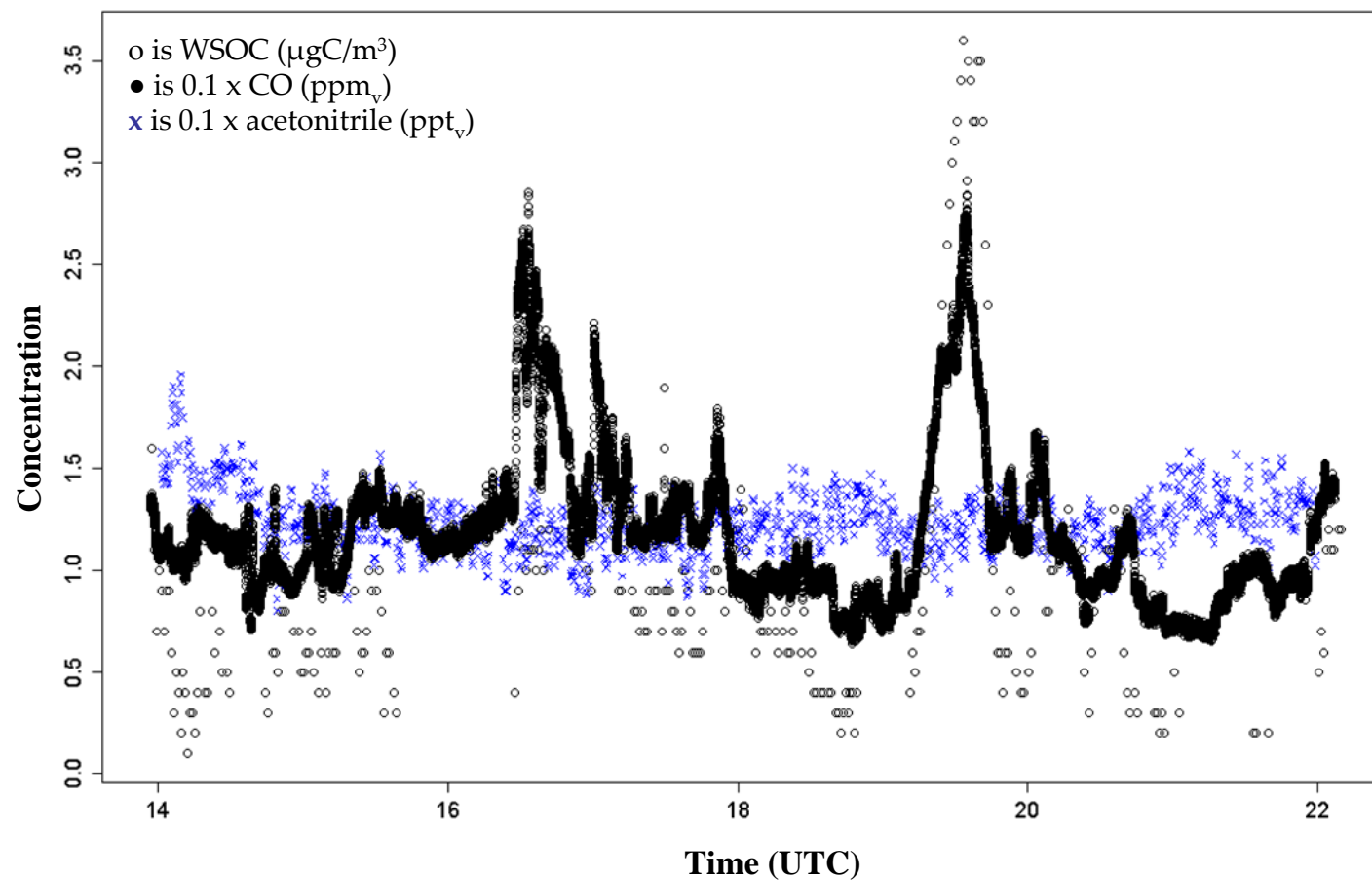


Figure S-2. WSOC, CO and acetonitrile measurements during the August 14th NOAA-P3 flight. The WSOC/CO covariance at ~19 UTC suggests an urban plume. The lack of covariance of WSOC/acetonitrile suggests little influence of a fire plume (7).

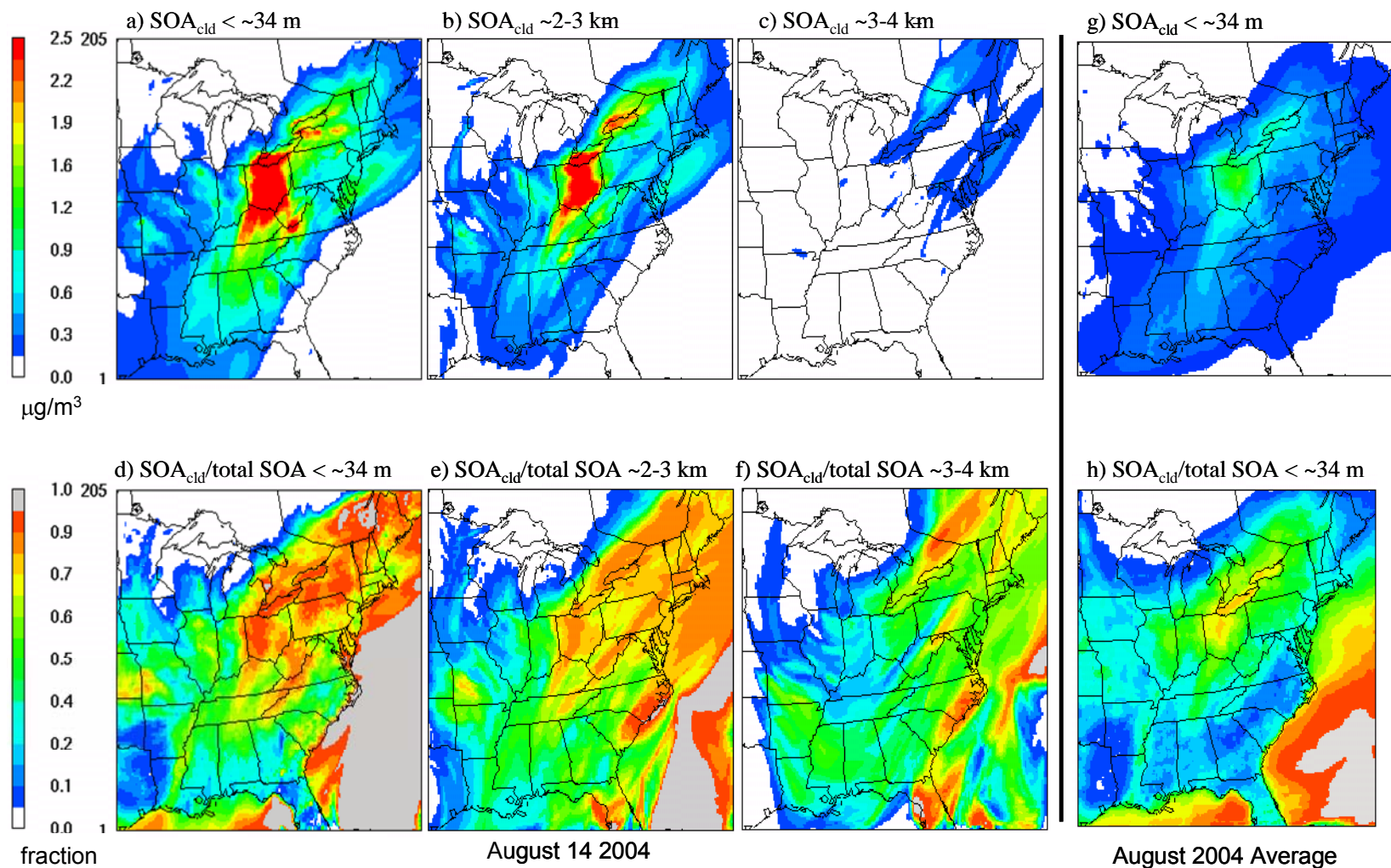


Figure S-3. SOA_{cld} Concentrations and Fractions. 24-hour average CMAQ predicted SOA_{cld} on August 14, 2004 (a) in the surface layer, (b) at $\sim 2\text{--}3 \text{ km}$ (typical of P3 flights on August 14), (c) $\sim 3\text{--}4 \text{ km}$. 24-hour average fraction of total SOA that is SOA_{cld} at d) the surface layer, e) $2\text{--}3 \text{ km}$ and f) $3\text{--}4 \text{ km}$. Figures S-1(g) and (h) are averages for August 2004. Note that SOA_{cld} concentrations and patterns change over the domain and day-to-day as do clouds. Higher SOA_{cld} fractions over the ocean may be related to transport.

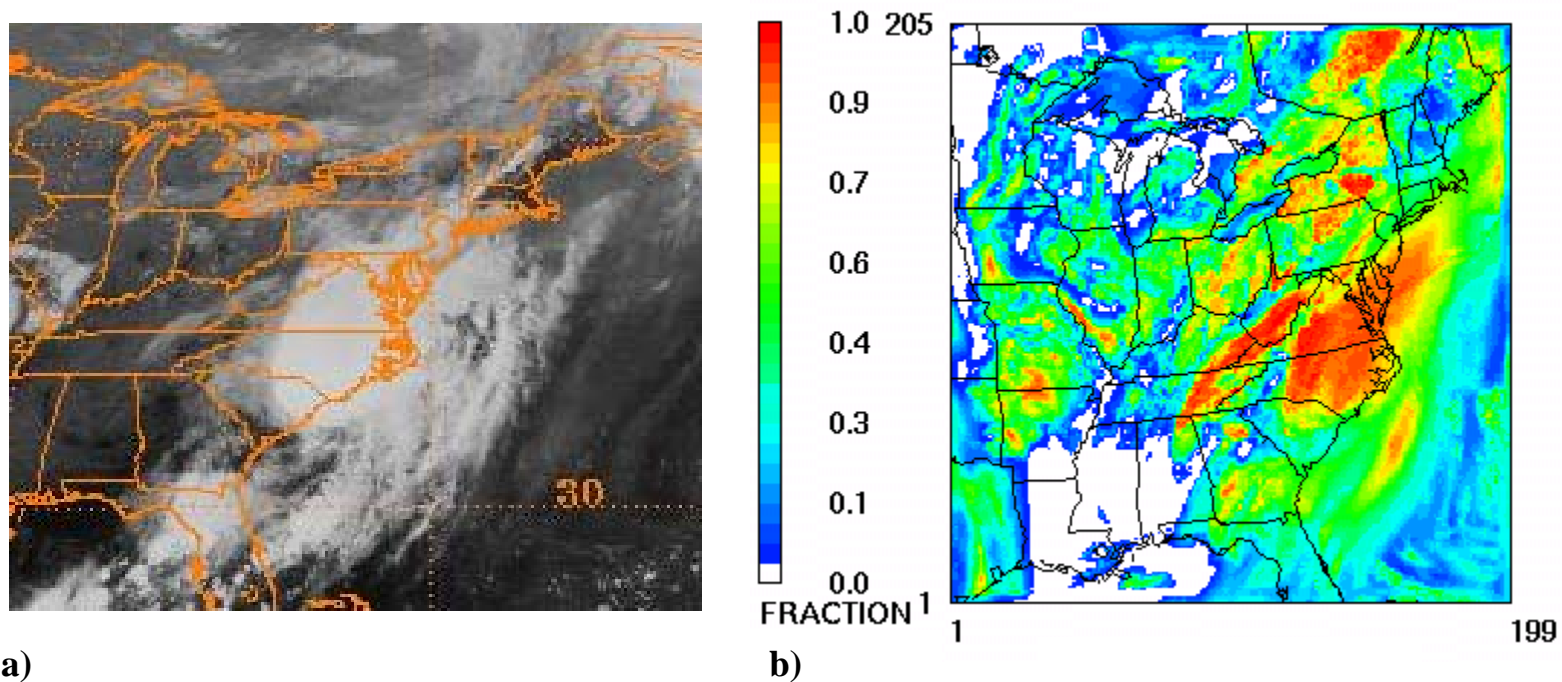


Figure S-4. GOES satellite image from the national climatic data center for August 14, 2004 at ~ 15 UTC (a) <http://ncdc.noaa.gov/oa/satellite.html>. CMAQ-predicted cloud fraction averaged over the P3 flight (b). Note general agreement between widespread cloud cover observations and predictions for the time and area. Note that vertical boundaries do not have a downward flux into the domain.

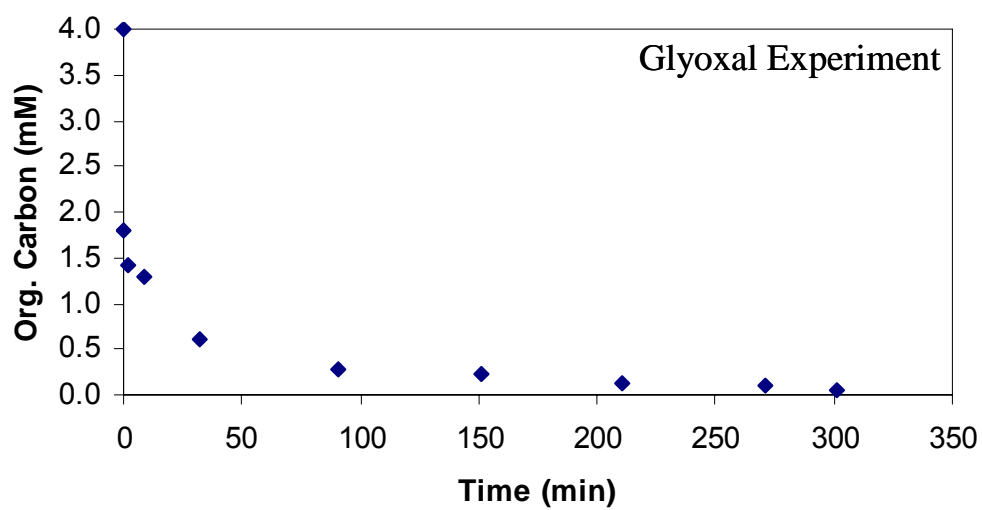


Figure S-5. Total Organic Carbon (TOC) measurements in aqueous experimental samples from glyoxal photooxidation experiments. As CO₂ forms organic carbon concentration decreases.