5.4 HIGH RESOLUTION MODELING OF OXIDANTS AND AEROSOLS DURING THE 1999 NE-OPS FIELD CAMPAIGN IN PHILADELPHIA

Jerome D. Fast
Pacific Northwest National Laboratory, Richland, Washington

1. INTRODUCTION

A nested meteorological-chemical modeling system is used to simulate the evolution of oxidants and aerosols around Philadelphia. Surface and airborne meteorological and chemical measurements made during a 30-day period in July and August of 1999 as part of the Northeast Oxidant and Particulate Study (NE-OPS) field campaign (Philbrick et al., 2002) are used to evaluate the performance of the modeling system. In a previous study (Fast et al. 2002; Fast 2002), a 24-km simulation domain was employed to determine the relative contribution of regional and local sources on ozone concentrations. The model demonstrated that upwind vertical mixing processes the previous afternoon, subsequent horizontal transport aloft, and depletion of ozone by NO titration within the stable boundary layer at night lead to the development of layers of ozone aloft observed during the morning. Through a series of sensitivity studies, most of the ozone was the result of emissions in the vicinity of Philadelphia and Chesapeake Bay area, but up to 30-40% of the ozone during high ozone episodes was due to transport from upwind sources.

This study expands upon the previous work by 1) adding a 4-km grid that encompasses the urban corridor between Washington D.C. and New York City and 2) including aerosols. While a 24-km grid was sufficient to simulate the regional-scale processes that affected the multi-day evolution of ozone in Philadelphia, a 4-km grid is needed so that local spatial and temporal variations in ozone and ozone precursors can be compared to aircraft measurements. The relative role of urban, rural, and point emission sources on the spatial distribution of pollutants around Philadelphia is examined. The effect of the predicted local wind field and boundary layer depth on the simulated evolution of ozone and ozone precursors is discussed.

2. FIELD CAMPAIGN MEASUREMENTS

Researchers from the U.S. Department of Energy's Argonne National Laboratory, Brookhaven National Laboratory, and Pacific Northwest National Laboratory participated in the NE-OPS field campaign between 23 July and 11 August, 1999. Chemical measurements were obtained from routine surface monitoring stations, DOE's Gulfstream-1 (G-1) aircraft (Kleinman et al., 2002), ozonesondes (Fast et al, 2002) and special surface instrumentation (Marley and Gaffney, 2002).

Routine meteorological data were supplemented with additional measurements collected from an array of

*Corresponding author address: Jerome D. Fast, Pacific Northwest National Laboratory, P.O. Box 999, K9-30, Richland, WA 99352, e-mail:jerome.fast@pnl.gov

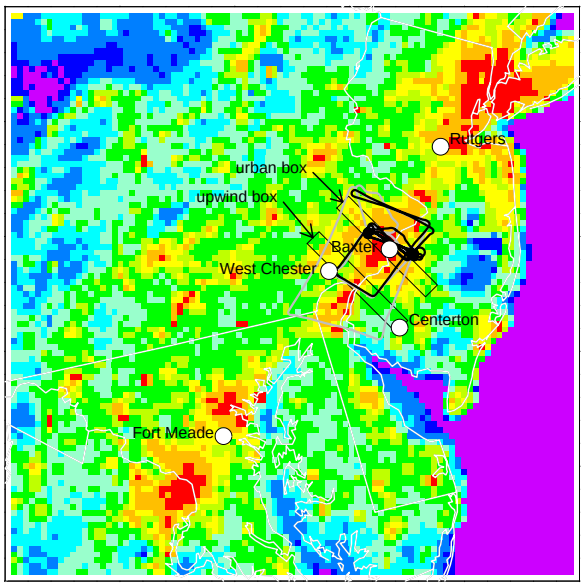

Fig. 1. NOx emission rates over the 4-km computational grid (color), G-1 flight path on the morning (thick black line) and afternoon (thick gray line) of 31 July 1999, and main measurement sites during NE-OPS 1999 (white dots). NOx emission rates vary from low (purple) to high (red) values. Thin lines denote boxes used in Figs. 5 and 6 to compare model output with aircraft data. The domain size is 384 x 384 km.

radar wind profilers, a sodar, and radiosondes Three 915 MHz radar wind profilers were located at the Baxter, West Chester, and Centerton sites (Fig. 1). The Baxter site was located in an urban area along the Delaware River northeast of downtown Philadelphia. The West Chester site was located in a suburban area on the campus of West Chester University about 35 km west of Baxter and the Centerton site was located in a rural area about 50 km south of Baxter. The West Chester and Centerton sites were chosen to bracket the expected path of the urban plumes transported over Philadelphia by southwesterly flow associated with a Bermuda high. Two operational radar wind profilers at Fort Meade and Rutgers provided additional wind profiles along the mid-Atlantic coast. Radiosondes were released fives times a day from the Baxter and Centerton sites on days in which the G-1 aircraft was making measurements.

3. MODEL DESCRIPTION

The PNNL Eulerian Gas and Aerosol Scalable Unified System (PEGASUS) as described in Fast et al., 2002) was employed to provide additional insights into the processes important to the transport and mixing of ozone during NE-OPS 1999. PEGASUS is a one-way

coupling of a mesoscale meteorological model and a chemical transport model where both models employ the same computational grid. In this study, three nested grids were employed. The first grid encompassed most of eastern North America with a grid spacing of 48 km. The second grid encompassed the northeastern U.S. with a 24-km grid spacing and the third grid, shown in Fig. 1, encompassed the mid-Atlantic region with a grid spacing of 4 km. The vertical grid spacing was 25 m adjacent to the surface that gradually increased to 600 m near the model top at 20 km. Due to the staggered vertical coordinate, the first node was at 12.5 m AGL. Hourly emission rates of 14 trace gas species were obtained from the SMOKE model (Houyoux et al., 2000) and the spatial distribution of NOx emission rates over the 4-km grid at 12 UTC 15 July 1999 is shown in Fig. 1.

Three significant modifications have been made to PEGASUS recently. First, aerosols are now simulated using a sectional approach for the both mass and number and the moving-center size structure is employed to solve the dynamic equations that describe the size and composition of the aerosols (Zaveri et al. 2002). Second, the treatment of convective vertical mixing has been changed to include a module that simulates vertical mixing, cloud chemistry, and wet removal processes similar to the RADM (Dennis et al., 1993] and CMAQ (Roselle and Binkowski, 1999). Both precipitating (deep) and non-precipitating (shallow) convection are simulated, and they can coexist with stratiform clouds. Third, photolysis rates have been updated using the scheme described by Wild et al. (2000) that is dependent on the predicted cloud, ozone, and aerosol profiles

The model was run for a 30-day period between 12 UTC 15 July and 12 UTC 14 August 1999. Application of a four-dimensional data assimilation technique was used to limit forecast errors in the meteorological fields. 4DDA nudged the u- and v-components of the wind, the potential temperature, and the specific humidity into closer agreement with the 6-h analyses from the National Center for Environmental Prediction's AVN model. The special meteorological measurements made during the field campaign were not incorporated by the 4DDA procedure so that they could be used as an independent data set to evaluate the model.

In this paper, only the model results for 31 July 1999 are shown. The weakest ambient winds during the 30-day period occurred on this day. Radar wind profiler measurements showed that the winds within several hundred meters of the ground were usually from the southwest at less than 2 m s^{-1}, but periods of light and variable winds occurred as well. Northwesterly winds around 5 m s^{-1} were observed at 1.5 km above ground level (AGL), but the speeds at this elevation were still lower than most other days during the 30-day period. The stagnant meteorological conditions contributed to ozone mixing ratios exceeding 120 ppb at many monitoring stations along the northeast urban corridor. This day is chosen to illustrate the effect of model errors in the local wind field and boundary layer depth on the spatial and temporal evolution of ozone and ozone precursors around Philadelphia during stagnant conditions. At the conference, results from the 4-km grid for the entire 30-day period will be presented.

4. RESULTS

Since the grid configuration, boundary conditions, and data assimilation procedures in this study was similar to Fast et al. (2002) with the exception of the additional 4-km grid, the predicted wind and temperature profiles were similar those reported in that study and the observed values. The overall time evolution of ozone from 11 monitoring stations within 50 km of the Baxter site and the model results over the same area were also similar during the entire 30-day period. As expected, the 4-km simulation produced more spatial variability in the concentrations of ozone than the 24-km simulation. For example, the surface ozone distribution at 21 UTC (16 LST) 31 July 1999 is shown in Fig. 2. Both the model and the observations indicated ozone mixing ratios exceeding 120 ppb between Washington D.C. and New York City at many locations, with lower mixing ratios between 40 and 60 ppb to the west over the Appalachian Mountains. Ozone was under-predicted at several stations northeast of Baltimore and southwest of Philadelphia. These under-predictions were likely due to local transport errors that will be discussed later. Some of the spatial variations in ozone, such as the small areas of ozone less than 70 ppb along the Delaware River, are associated with stack emissions. High NO emission rates from the point sources tend to reduce ozone near the source and increase ozone several km downwind.

Differences between the 24 and 4-km simulations were also evident aloft. As shown in Figs. 3 and 4, the predicted range of ozone and NOy are compared with the G-1 aircraft measurements. The 24-km simulation produced a range of ozone mixing ratios around Philadelphia that was similar to the measurements aloft. However, the NOy mixing ratios were as much as 35 ppb too low around 500 m AGL. The 4-km simulation, however, produced a range of ozone and NOy mixing ratios that were both similar to the observed profiles.

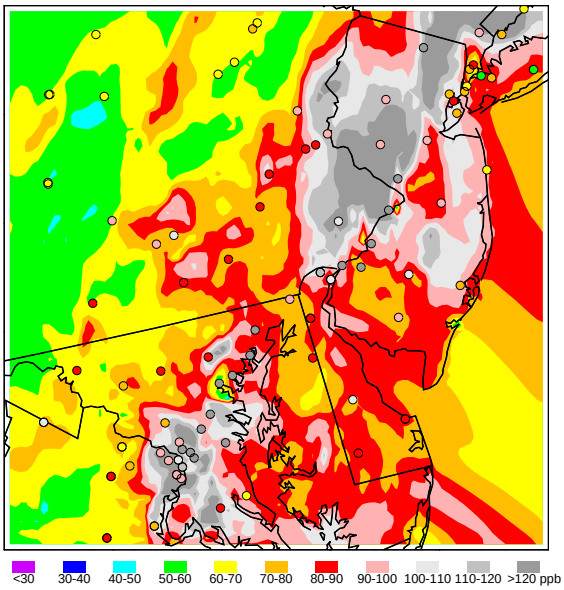

Fig. 2. Observed (dots) and simulated surface ozone (contours) over the 4-km grid at 19 UTC 31 July 1999.

This indicates that the emissions spread evenly over the 24-km grid cells smoothed out the precursor concentration of faster reacting species.

While the 4-km simulation produced a range of ozone and ozone precursors at the surface and aloft around Philadelphia that was similar to observed, a more critical evaluation of the model results are presented next to examine the local-scale transport and mixing processes and their effect on the distribution of trace gases. A comparison of the observed spatial distribution of ozone and NOy and the simulated values averaged over the "urban" and "upwind" boxes depicted in Fig. 1 is shown in Figs. 5 and 6. These aircraft flight legs were also examined by Kleinman et al. (2002).

During the morning of 31 July, the model produced a layer of ozone over Philadelphia (Fig. 5) between 0.5 and 1.2 km AGL with peak values around 85 ppb. This layer was produced the previous afternoon from precursor emissions in the vicinity of Philadelphia. While the pea ozone mixing ratios were similar to the measurements along the lower flight leg, the ozone mixing ratios aloft between 1.5 and 2.5 km were 10 to 20 ppb too high. The NOy mixing ratios were too large within 1 km of the ground, but close to the measurements at higher elevations. During the day, the layer of ozone was entrained into the growing convective boundary layer contributing to ozone produced by precursors emissions that day. By the afternoon, simulated ozone mixing ratios in the convective boundary increased to just over 120 ppb. Ozone mixing ratios greater than 120 ppb were measured by the G-1 near the Delaware River, but the simulated values occurred a few km to the north. The simulated NOy mixing ratios along the lower flight leg were close to the measurements, but the simulated concentrations at higher elevations were too low.

Some of the differences between the observed and simulated ozone and NOy distributions can be attributed to errors in the predicted vertical mixing processes during the day and night. During the night of 30 and 31 July, vertical mixing processes over Philadelphia transported surface ozone precursors above the stable boundary layer, producing concentrations of NOy that were larger than observed during the morning of 31 July. During the afternoon of 31 July, G-1 aircraft profiles indicated that at elevations above 1.5 km higher ozone and NOy mixing ratios occurred north of the Delaware River. These measurements suggest that the convective boundary layer was deeper north of the Delaware River over the more densely build-up areas. Significant local spatial variations in the convective boundary layer between urban and rural areas over Nashville were also found by Banta et al. (1998) during the 1995 Southern Oxidants Study. While the model produced local spatial variations in the mixed layer depth of a few hundred meters, a deeper convective boundary layer was not simulated over Philadelphia since the mesoscale model does not have an urban canopy parameterization.

Errors in the predicted wind fields also produced differences between the observed and simulated ozone and NOy distributions. The observed winds were light and variable during the afternoon, but the simulated winds were southerly at 2 m s^{-1}. Consequently, the

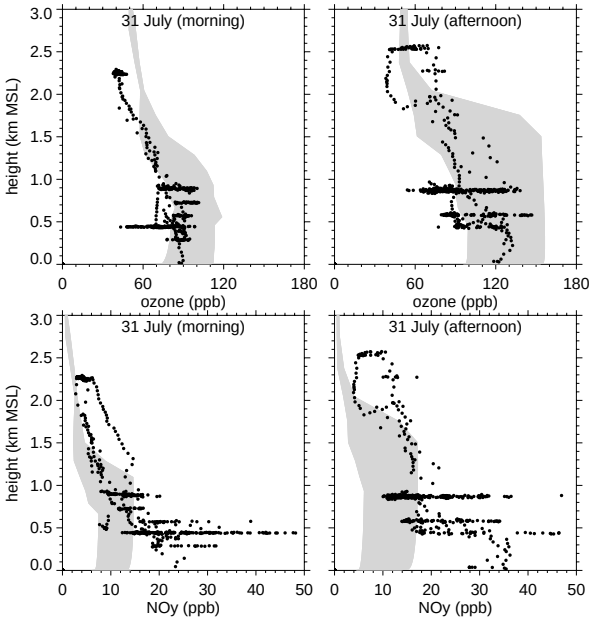

Fig. 3. Observed ozone from the G-1 aircraft (dots) on 31 July 1999 and simulated range of ozone (shading) in a vertical column within 48 km of Baxter from the 24-km grid. The simulated range of values also encompasses the flight periods that were between 9 and 11 LST (morning) and 14 and 16 LST (afternoon).

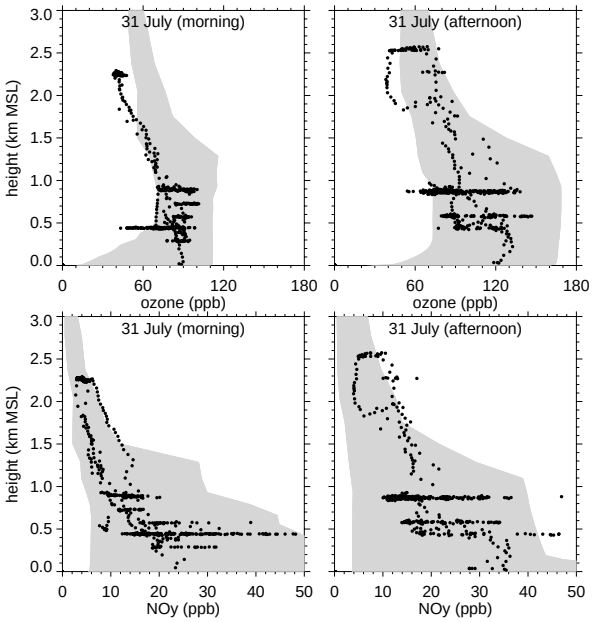

Fig.4. Same as Fig.2, except the simulated range is from the 4-km grid.

simulated ozone plume moved too far northward as shown in Fig. 2. Mesoscale models cannot simulate light and variable wind conditions; however, small wind

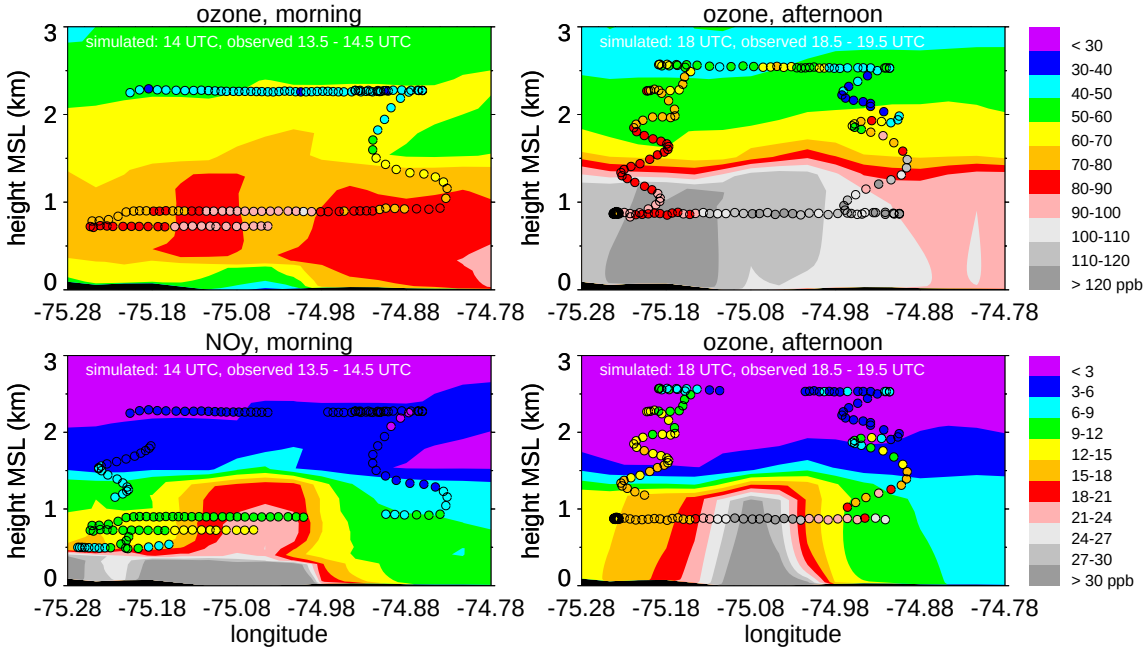

Fig. 5. Vertical cross section of simulated ozone and NOy within the "urban" box (see Fig. 1) and the aircraft measurements along the northwest to southeast flight paths within and adjacent to the box. Observed and simulated quantities during the morning and afternoon flight periods are shown on the left and right, respectively.

direction errors over several hours lead to significant horizontal transport errors on this day.

As discussed in Kleinman et al (2002), evidence of a large point source emission was observed by the G-1 upwind of Philadelphia. In the morning, ozone dropped sharply along the "upwind" flight leg (Fig. 1) while ozone precursors increased. A broader band of ozone and NOy was observed as the G-1 passed over the area during the afternoon. As shown in Fig. 6, the model also simulated an increase in ozone precursors near the point source, but the mixing ratios were 10 ppb to low and only a slight decrease in ozone occurred. The 4-km grid spacing was still too large to represent fast reactions and resolve horizontal mixing near point sources. By the afternoon, the simulation ozone and NOy distributions were qualitatively similar to the observations, although the NOy concentrations were still too low in this region. The broader distribution in the model and the measurements were likely produced by multiple emission sources in the area that mixed during the afternoon hours.

Another factor contributing to differences between the ozone and ozone precursor distributions in the "urban" and "upwind" boxes was the growth rate of the convective boundary layer. Simulated values one hour before or after the times shown in Figs. 5 and 6 were sometimes closer to the G-1 measurements. For example, NOy concentrations below 400 m AGL m at 14 UTC within the "upwind" box were 5 to 10 ppb higher than at 15 UTC.

While the mesoscale model qualitatively produced the light wind conditions observed on 31 July, the simulated trace gas fields illustrated that small errors in both the horizontal winds and vertical mixing processes complicate the direct comparison of model output aircraft data. On days in which the synoptic winds were stronger, there was a better agreement between observed and simulated quantities along the G-1 flight paths.

5. SUMMARY

The model qualitatively simulated the evolution of ozone and ozone precursors in the vicinity of Philadelphia during 1999 NE-OPS field campaign. Differences between the observations and the 4-km simulation demonstrated the effects of transport and vertical mixing errors on predictions of ozone and ozone precursors. These errors were most evident when the synoptic forcing was weak and the ambient winds were light and variable, such as on 31 July 1999. When the synoptic forcing was stronger, the model performance improved at the surface and aloft. By the time of the conference, the 4-km simulation will be repeated so that 4DDA includes the profiler observations to further quantify the local transport errors.

Acknowledgments. I would like to thank the G-1 aircraft pilots and flight crew and scientists from ANL, BNL, PNNL, West Chester University, Rutgers University, Environment Canada, University of Maryland, and North Carolina Supercomputing Center for providing data and assistance. Rahul Zaveri, Richard Easter, Elaine Chapman, Jim Barnard , and Xindi Bian contributed to the development of PEGASUS. This research was supported by the U.S. DOE, under the auspices of the Atmospheric Chemistry Program of the Office of Biological and Environmental Research, under Contract DE-AC06-76RLO 1830 at the PNNL. PNNL is operated for the U.S. DOE by Battelle Memorial Institute. The Gulfstream-1 aircraft is owned by Battelle Memorial Institute and operated by PNNL for the U.S. DOE.

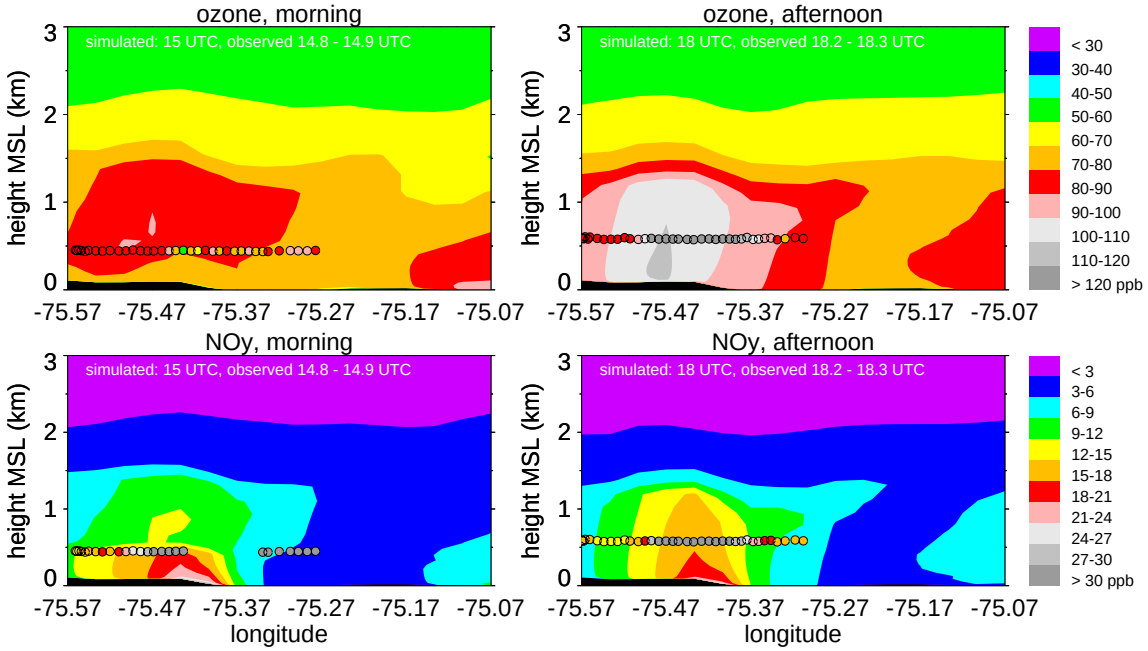

Fig. 6. Same as Fig.5, except for the "upwind" box (see Fig. 1).

REFERENCES

Banta R.M., C.J. Senff, A.B. White, M. Trainer, R.T. McNider, R.J. Valente, S.D. Mayor, R.J. Alvarez, R.M. Hardesty, D. Parrish, and F.C. Fehsenfeld, 1998: Daytime buildup and nighttime transport of urban ozone in the boundary layer during a stagnation episode. *J. Geophys. Res.*, 103, 22519-22544.

Dennis, R.L., J.N. McHenry, W.R. Barchet, F.S, Binkowski, and D.W. Byun, 1993: Correcting RADM's sulfate underprediction: Discovery and correction of model errors and testing the corrections through comparisons against field data. *Atmos. Environ.,* 27A, 975-997.

Fast, J.D., 2002: The relative role of local and regional-scale processes on ozone in Philadelphia. *4th Conf. on Atmos. Chem.*, Amer. Meteor. Soc., Orlando FL, 121-124.

Fast, J.D, R.A. Zaveri, X. Bian, E.G. Chapman, and R.C. Easter, 2002: The effect of regional-scale transport on oxidants in the vicinity of Philadelphia during the 1999 NE-OPS field campaign. *J. Geophys. Res.*, 107 (D16), 10.1029/2001JD000980.

Houyoux, M.R., J.M. Vukovich, C.J. Coats, N.W. Wheeler, and P.S. Kasibhatla, 2000: Emission inventory development and processing of the Seasonal Model for Regional Air Quality (SMRAQ) project. *J. Geophys. Res.*, 105, 9079-9090.

Kleinman L.I. et al., 2002: Ozone production in the Philadelphia urban area during NEOPS 99. *4th Conf. on Atmos. Chem.*, Amer. Meteor. Soc., Orlando FL, 140-145.

Marley, N.A., and J. S. Gaffney, 2002: Northeast oxidant and particulate study (NEOPS). *4th Conf. on Atmos. Chem.*, Amer. Meteor. Soc., Orlando FL, 115-120.

Philbrick, C.R., et al., 2002: Overview of the NARSTO-NE-OPS program. *4th Conf. on Atmos. Chem.*, Amer. Meteor. Soc., Orlando FL, 107-114.

Roselle, S., and F. Binkowski, 1999: Cloud dynamics and chemistry, in *Science Algorithms of the EPA Models-3 Community Multiscale Air Quality (CMAQ) Modeling System*. Edited by D. W. Byun and J. K. S. Ching, U.S. EPA report EPA/600/R-99/030.

Wild, O., X. Zhu, and M.J. Prather, 2000: Fast-J: Accurate simulation of in- and below-cloud photolysis in tropospheric chemical models. *J. Atmos. Chem.*, 37, 245-282.

Zaveri R.A., Easter R.C., and Peters L.K., 2002: Development of a new model for simulating aerosol interactions and chemistry. Manuscript in preparation.