

Comparisons of Model Aerosol Mass and Chemical Composition with Observations from the 2002 New England Air Quality Study

G. J. FROST*, S. A. MCKEEN*, A. MIDDLEBROOK, J. DEGOUW*, E. WILLIAMS*
NOAA Aeronomy Laboratory, Boulder, CO, USA

S. E. PECKHAM*, G. GRELL*
NOAA Forecast Systems Laboratory, Boulder, CO, USA
**Also with CIRES, University of Colorado, Boulder, CO, USA*

R. SCHMITZ
*Department of Geophysics, University of Chile, Santiago, Chile, and IMK-IFU, Forschungszentrum
Karlsruhe, Garmisch-Partenkirchen, Germany*

R. TALBOT
EOS, University of New Hampshire, Durham, NH, USA

P. K. QUINN, T. S. BATES
NOAA Pacific Marine Environmental Laboratory, Seattle, WA, USA
M. CANAGARATNA, D. WORSNOP
Aerodyne Research Inc, Billerica, MA, USA

1. Introduction

The 2002 New England Air Quality Study (NEAQS 2K2) was designed to provide a better understanding of factors controlling air quality in the northeastern United States (<http://www.al.noaa.gov/NEAQS/>). The study sought to address the role of long-range transport of pollutants to New England, quantification of local emissions, the effect of land and sea breezes on air quality in the region, the evaluation of the capabilities of current air quality forecasting systems, and the linkage between air quality and climate.

NEAQS 2K2 provided an opportunity to evaluate WRF-Chem (Weather Research Forecast model with on-line chemistry and aerosols). In the present work, comparisons are made between ship-based observations and WRF-Chem forecasts carried out in support of NEAQS 2K2. The focus of this work is on the mass and chemical composition of aerosols with diameters below about 1 micron (sub- μm). Model-observation comparisons are also made for gas-phase tracers and precursors of condensable material in order to provide a context for understanding the particle results. These comparisons represent the first evaluation of WRF-Chem aerosol module forecasts with ambient observations.

2. Observations

The NEAQS 2K2 observations discussed here were made onboard the NOAA Research Vessel *Ronald H. Brown*. This work focuses on the period 22 - 25 July, 2002, which was a subset of the month-long NEAQS

2K2 cruise of the *Ron Brown*. The focus period was characterized by relatively clear skies with the exception of a rapid frontal passage on 7/23/02 at about 18Z, which brought cloudy skies and some rainfall to the region for a few hours. On 7/22/02 and 7/23/02, the ship made numerous transects through plumes moving in a generally northeast direction offshore from northern Massachusetts. On 7/24/02 the ship cruised northeast along the coast of New Hampshire and Maine, and on 7/25/02 sailed back along a parallel track to the coastal waters of northern Massachusetts. The first two days of the period were characterized by relatively polluted air observed on the *Ron Brown* due to both local and regional plumes, while during the latter two days the observations show relatively cleaner air.

The aerosol observations compared with model predictions include those of two instruments deployed on the *Ron Brown*. The Aerodyne Aerosol Mass Spectrometer (AMS) measured size-resolved, non-refractory (volatile) material in sub- μm aerosols with a frequency of one measurement every 2 minutes. The AMS sub- μm particle matter (PM) mass of sulfate (SO_4), ammonium (NH_4), nitrate (NO_3), and organics (OM) as well as the total mass across these 4 categories were examined here. The Particle-Into-Liquid Sampler (PILS) measured the total mass of various water soluble species in sub- μm aerosols; only the 15-min sulfate observations are discussed here. One-minute observations of gas-phase O_3 and SO_2 from the *Ron Brown* were also compared with WRF-

Chem results. In point-to-point comparisons with the model, all observations were averaged on the 1-hour timebase of the model output.

3. Model

During NEAQS 2K2 WRF-Chem was run in the configuration described in detail on the WRF Working Group 11 web site (<http://www.wrf-model.org/WG11/>). In particular, WRF-Chem was run at a horizontal resolution of 27 km with the RADM2 chemical mechanism (Stockwell et al., 1990; Chang et al., 1989) and anthropogenic emissions from the EPA NET 1996 inventory. Only the most recent of the three 36-hour forecasts available at any given hour was used in the comparisons described here.

The WRF-Chem aerosol module is based on the Modal Aerosol Dynamics Model for Europe (MADE) (Ackermann et al., 1998) which itself is a modification of the Regional Particulate Model (Binkowski and Shankar, 1995). Secondary organic aerosols (SOA) have been incorporated into MADE by Schell et al. (2001) by means of the Secondary Organic Aerosol Model (SORGAM). The module treats nucleation, condensation, coagulation and aerosol-phase chemistry assuming the aerosol size distribution is approximated by the sum of three log-normal functions. The model sub- μm PM mass discussed here is equal to the total masses in the Aitken and accumulation modes.

The RADM2 chemical mechanism does not carry monoterpenes (e.g., α -pinene), which are thought to be the predominant biogenic source of aerosols. Consequently, model predictions of organic and total PM mass were therefore expected to be lower than observed. In addition, the NEAQS 2K2 configuration of WRF-Chem included only gas-phase reactions to convert reduced gas-phase sulfur to aerosol sulfate. In-cloud S(IV) oxidation, which is thought to be a significant contributor to sulfate production, was not included.

4. Results and Discussion

WRF-Chem is able to capture the horizontal distribution, diurnal profile, and approximate magnitude of observed O_3 , indicating the large scale features of transport and gas-phase photochemistry are captured by the model. A linear regression of model vs observed O_3 yields a slope of 0.82 with a correlation coefficient r^2 of 0.57 for the entire NEAQS 2K2 data set. The model reproduces the difference

between the higher O_3 observed during 7/22/02 and 7/23/02 in more polluted air and the lower O_3 levels observed later in the focus period. WRF-Chem predicted the frontal passage on 7/23/02 but its predicted arrival time at the ship's position was late by several hours. The model predicts some of the observed fine structure in O_3 due to changes in the ship's position relative to outflow plumes on 7/23/02.

A comparison of the observed total sub- μm PM mass with that predicted by WRF-Chem (Figure 1) has some similar features to those seen with O_3 . Relative differences between the polluted first 2 days of the period, with their higher PM mass, and the cleaner final 2 days are reproduced by the model. The model has a later drop off in PM mass on 7/23/02 than the observations for the same reason as O_3 , namely the late predicted arrival of the front. Like in the case of O_3 , the model captures the observed decrease/increase in PM levels as the ship moves out of and into the 7/23/02 outflow. The AMS and PILS instruments measured very similar mass of total PM and of the aerosol species which both were able to measure.

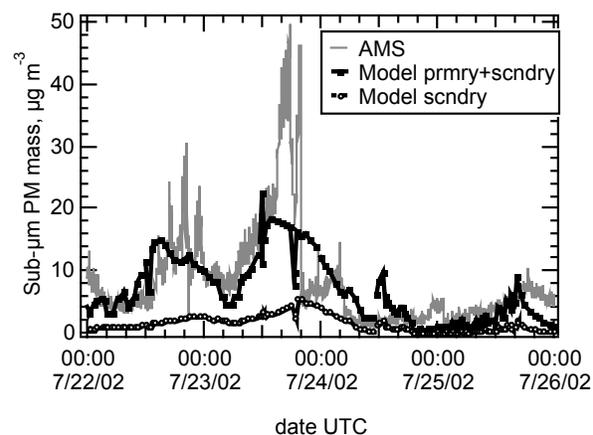


Figure 1. Total AMS sub- μm particle mass (gray line) and WRF-Chem predictions including both primary and secondary PM mass (black squares) and with just secondary mass (black circles).

Unlike O_3 , WRF-Chem predictions of PM mass are significantly lower than the observations. Figure 1 shows two model traces: a higher mass trace which includes both primary emitted PM (mostly from the unspicated NET-96 emissions category "PM2.5 Fine") and secondary, speciated aerosol mass, and a lower mass trace which includes only the speciated components, which are mostly secondary aerosol. Even when unspicated "PM2.5 Fine" mass is

included in the total, the model underpredicts the observations during the peak pollution periods. Linear regression of the model vs observed sub- μm mass for the full 2 weeks of model simulations gives a slope of 0.44 with r^2 of 0.26.

The high proportion of particle mass which is directly emitted ($\sim 70\%$) is in contrast to the observations, where the aerosol mass is predominantly secondary (Figure 2). Observed aerosol mass is divided mostly between roughly comparable amounts of sulfate and organics, both of which are significantly underpredicted by the model. The model also misses much of the fine structure in the observations caused by nearby point sources which are not sufficiently resolved by the model's 27-km grid (Figure 1).

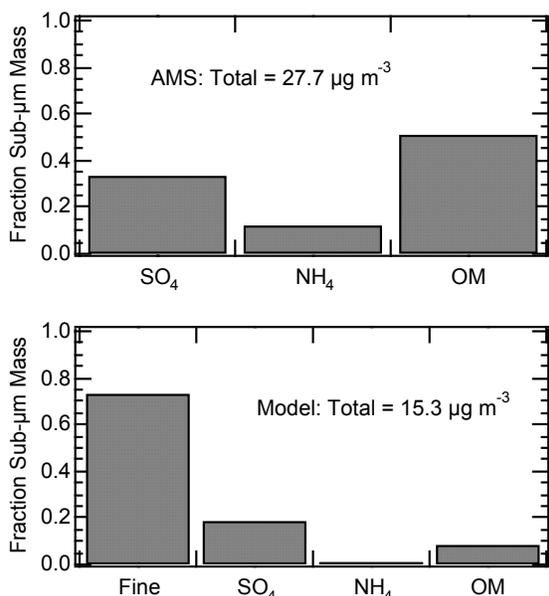


Figure 2. Average speciated fraction of sub-micron PM mass observed by the AMS (top) and predicted by WRF-Chem (bottom) on 7/23/02 between 14Z and 20Z.

Model predictions of the total sulfur concentration in the gas (SO_2) and aerosol (sulfate) phases indicates that model SO_2 emissions are in reasonable agreement with observations. The large power plant sources that cause elevated ambient SO_2 levels have relatively well-known emission strengths. The model predicts much lower ratios of aerosol sulfate to total sulfur than is observed throughout the focus period, however. The modeled S(IV) to S(VI) oxidation rate appears to be too slow. This result might have been expected, given the lack of an in-cloud sulfur oxidation scheme

in the model. The focus period was chosen because it was relatively cloud-free in the vicinity of the RV *Brown*, in the hope of minimizing the effects of omitting the in-cloud S(VI) production. However, since long-range transport of SO_2 is important, in-cloud oxidation can occur far upstream of the point of observation and affect sulfate budgets downwind.

Comparison of observed and modeled O_3 vs NO_y - NO_x correlations shows relatively good agreement (Figure 3, top). The model was able to capture both the rate and magnitude of rapid gas-phase conversion of precursors to O_3 . Observed and modeled secondary PM mass both show correlation with O_3 (Figure 3, bottom). However, the modeled production rate of secondary aerosol is about an order of magnitude slower than what is observed. This model underestimate likely results both from relatively slow sulfur oxidation as well as model underestimates of the production rate of organic mass from both anthropogenic and biogenic sources.

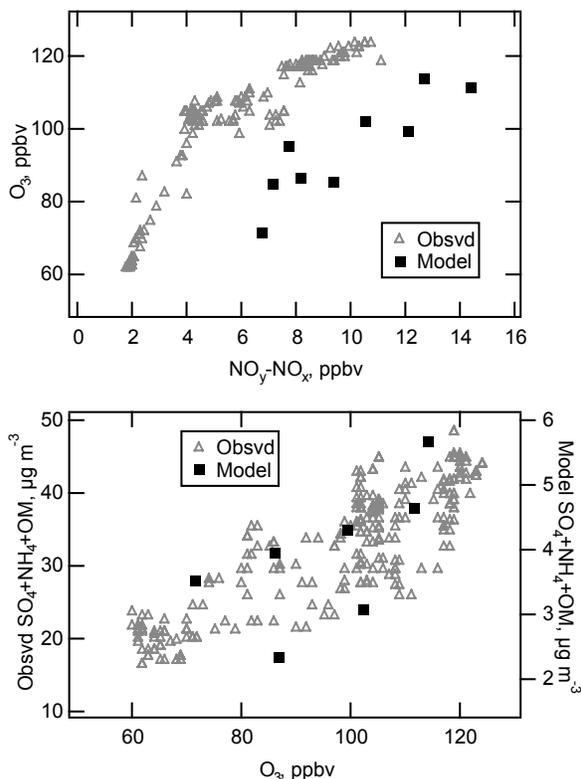


Figure 3. Observed and modeled O_3 vs NO_y - NO_x (top) and secondary PM mass vs O_3 (bottom).

5. Recommendations

These results indicate a number of steps that must be taken in future WRF-Chem evaluations. Higher model resolution should help improve the model's treatment of point source emissions near the location of observations. Emission inventories of particle matter must be more completely speciated into chemical components in order to understand the importance of primary vs secondary aerosol production and to test the accuracy of current inventories. Biogenic emissions of important aerosol precursors such as the monoterpenes must be coupled to the gas-phase chemical mechanism, which could be achieved by updating the RADM2 scheme to that of RACM (Stockwell et al., 1997). In-cloud sulfur oxidation must be accounted for within the model. Finally, further development of model VOC oxidation schemes may be needed to account for the significant levels of organics observed in aerosols.

Corresponding author:

Gregory Frost
NOAA Aeronomy Laboratory
325 Broadway, R/AL4, Boulder, CO, 80305, USA
E-mail: Gregory.J.Frost@noaa.gov

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