HIGH TIME-RESOLVED COMPARISONS FOR IN-DEPTH PROBING OF CMAQ FINE-PARTICLE AND GAS PREDICTIONS

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EPA/600/A-04/094

1. INTRODUCTION

In this paper, two major sources of bias in the Community Multi-scale Air Quality Model (CMAQ), one physical and one chemical process, are examined. The examination is conducted with hourly gas and particle data for the inorganic system of sulfate, total ammonia, also called NH_X, (gaseous ammonia, NH_3 plus aerosol ammonium, NH_4^+) and total nitrate (gaseous nitric acid, HNO_3 plus aerosol nitrate, NO_3^-) and with hourly gas and particle data for inert or conservative species. The physical source of bias stems from the meteorological inputs related to mixing, in particular the behavior of the simulated mixed layer in the evening. The chemical source of bias stems from the nighttime heterogeneous production of HNO_3 from N_2O_5. The analyses are carried out for a summer and a winter period to examine the seasonal dependence of the biases.

2. GENERAL MODEL AND DATA DESCRIPTION

2.1 CMAQ

CMAQ is an Eulerian model that simulates input of precursor emissions and atmospheric transport, transformation, and deposition of photochemical oxidants (ozone), particulate matter, airborne toxics and acidic and nutrient species (Byun and Ching, 1999). The 2004 release version of CMAQ was used for these simulations. The meteorological fields were derived from MM5, the Fifth-Generation Pennsylvania State University/National Center for Atmospheric Research Mesoscale Model (Grell et al., 1994) with data assimilation and use of the Pleim-Xiu land-surface model (PX) option (Pleim and Xiu, 1995). The modeling domain covered the contiguous U.S. with a 36-km horizontal grid dimension. A 24-layer vertical layer structure was used that reached to

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the top of the free troposphere. The simulations were performed with the SAPRC99 gas-phase chemical mechanism, with the U.S. EPA 2001 National Emissions Inventory and biogenic emissions from BEIS 3.12. Two periods corresponding to EPA Supersite Program intensives were simulated: July 2001 and January 2002.

2.2 Observational Data

The data used are high time resolution gas and particle data from July 2001 and January 2002 taken at two supersites in the EPA Supersite Program: Jefferson Street, Atlanta, a Southeastern Aerosol Research and Characterization Study (SEARCH) site (web address in references) and Schenley Park, Pittsburgh (Wittig et al., 2004; Takahama et al., 2004). In addition, companion (SEARCH) sites in the Southeastern US. were used.

3. RESULTS

3.1. Bias Stemming from Physical Process

Previous comparisons of CMAQ predictions of conservative species against data taken in 1995 in Nashville, TN (as part of the Southern Oxidant Study (SOS)) indicated that there was a systematic nighttime over-prediction of conservative species in the model. Comparison of simulations of mixing heights from MM5 (using the PX land-surface model option) and from radar profilers around Nashville indicated: (1) that the mixed layer heights were in good agreement during the mid-day and (2) that the mixed layer in MM5 was collapsing too soon in the late afternoon. It was hypothesized that the premature collapse of the boundary layer was contributing significantly to the nighttime over-predictions.

Comparisons against aircraft spirals over surface sites also indicated that during the day the atmosphere is well mixed and the surface concentrations are representative of the overall column concentration levels. Because pollutants in CMAQ are very well mixed in the vertical and the mixed layer heights appears to be in reasonable agreement when using the PX option with MM5, we expect the mid-day predicted and measured concentrations to be in good agreement when daytime emissions are reasonably correct.

If there is a premature collapse of the mixed layer, we expect a very rapid rise in predicted surface air concentrations leading to an over-prediction or positive bias in the late afternoon across many inert (e.g., CO and elemental carbon (EC0) or quasi-inert species (e.g., NO_Y and NH_X) that are emitted late in the day and at night. The key here is the rate of increase from mid-day levels. We expect little to no effect for species such as sulfate whose gas-phase formation shuts down as the sun goes down.

We start with EC as the example inert tracer. The average diurnal pattern of EC predictions and measurements at the Atlanta supersite location at Jefferson Street is shown in Figure 1a for July 2001 (summer) and 1b for January 2002 (winter). To better illustrate the relative afternoon rate of increase, the scales are adjusted so that the mid-day levels for model and measurements match. Indeed, we find a very rapid rise in surface air concentrations and a rapid increase in bias in the late afternoon. The bias is most pronounced in summer and least in winter. We will explain why later in this section.

The Atlanta diurnal patterns for CO and NO_Y (not shown) are very similar in each season to that in Figure 1 for EC. There appear to be nighttime sources of CO, EC and NO_X, consistent with diesel emissions, close to this site that are important in the winter and affect the nighttime comparisons. Diesel emissions are implicated because the EC to NO_Y relationship of the nighttime emissions is the same as for the AM and PM drive peaks. These sources are either not in the emissions inventory or not handled well by the chemical transport model. Figure 2 shows the diurnal pattern of EC comparisons in Pittsburgh for summer to show the similarity in another urban area (without the nighttime local source issue). Figures 3 shows the Pittsburgh diurnal patterns for SO_4^{2-} for summer, indicating that, as expected, sulfate concentrations are not seriously affected, because the SO_4^{2-} gas-phase production shuts down as the OH levels go to near zero in the evening. The winter diurnal comparison is very similar but with a slight sulfate over-prediction.

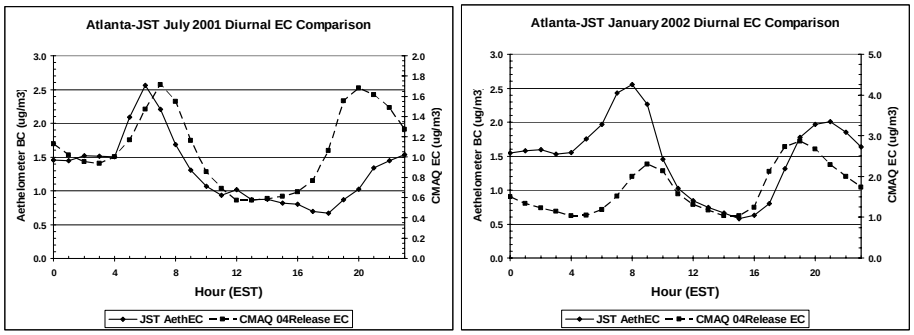

Figure 1. Comparison of the observed Athelometer Black Carbon and predicted Elemental Carbon hourly diurnal pattern based on a monthly average of each hour at Atlanta for (a) July 2001 and (b) January 2002.

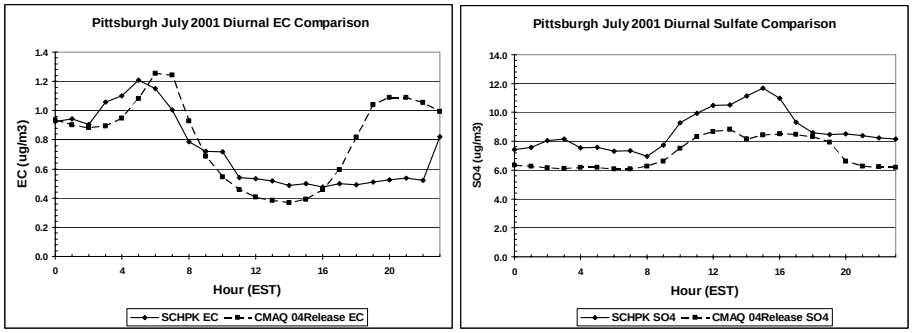

Figure 2. Comparison of diurnal pattern of EC at Pittsburgh for July 2001

Figure 3. Comparison of diurnal pattern of sulfate at Pittsburgh for July 2001

Figure 4 shows the monthly-averaged diurnal temperature bias for MM5 for July 2001 for Atlanta, Pittsburgh and the continental area of the Eastern U.S. excluding Florida. Given the regular diurnal pattern in the summer of the rise and collapse of the

boundary layer and the subsequent decrease in wind speed, we expect the temperature bias to provide a good indication of what is happening in the boundary layer. For Atlanta and Pittsburgh, the temperature bias goes positive at mid-day and then steadily falls to negative values shortly after 1600 EST and continues declining until 1900 EST and then reverses direction. We associate this rapid over-cooling in the MM5 with the premature collapse of the mixed layer. Interestingly, the pattern of cold bias maximum in the morning and afternoon is seen to be a systematic feature across the entire Eastern US. So we expect this issue of evening over-prediction to be present across the entire model domain. We expect Pittsburgh and Atlanta, with their larger swings in temperature bias, to be representative of urban areas; thus, we expect this issue to have to strongest effect in urban areas. In winter there is a flat, smooth temperature bias with only a monotonic rise towards no bias during the day and then a monotonic fall again to a constant evening bias level. In winter there is more competition between winds (mechanical turbulence) and density stratification and the atmosphere is less stationary, hence, the atmosphere does not become stable as often (or reaches that state much later in the evening). Thus, we expect less of an impact on the mixed layer and, hence, the impact on surface concentrations is expected to be less in winter than in summer.

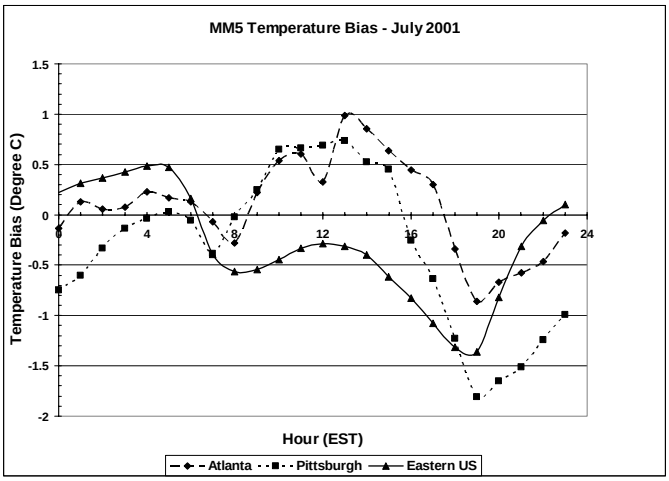

Figure 4. Plot of the monthly averaged hourly diurnal pattern of MM5 temperature bias for July 2001 at Atlanta, Pittsburgh and across the Eastern U.S.

Figure 5a presents the July 2001 diurnal pattern of NH_X in Pittsburgh, where there is a strong diurnal swing in the CMAQ predictions with under-prediction during the day and over-prediction at night, whereas there is little to no diurnal variation in the measurements. Figure 5b shows that the agreement between the 24-hour average predictions and observations looks fairly good; however, the daily averages have covered up the fact that there are compensating errors involved, possibly raising questions about emissions. The 24-hour averages also cover up the fact that the diurnally varying NH_X errors will significantly affect the partitioning of total-nitrate to aerosol nitrate, creating a companion bias for particulate nitrate. The exact same behavior of compensating errors

was seen with the August 1999 Atlanta supersite comparisons for EC, raising questions about the accuracy of the EC emissions - questions that would be missed when only looking at daily averaged concentrations. Figure 5c shows that there are also larger diurnal swings in the January 2002 predictions of NH_X for Pittsburgh compared to the data, with peaks in the morning and afternoon. Although not as dramatic as the summer situation, these diurnal swings will affect the total-nitrate partitioning as well.

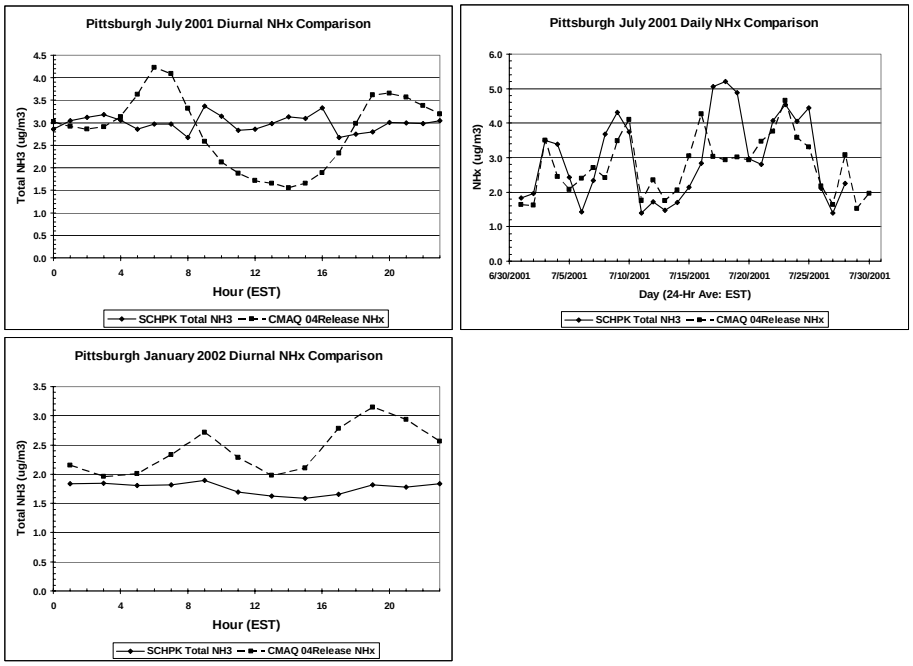

Figure 5. Comparison of the observed and predicted NH_X at Pittsburgh for (a) monthly averaged hourly diurnal pattern in July 2001, (b) daily 24-hour average in July 2001, and (c) monthly averaged hourly diurnal pattern in January 2002.

3.2. Bias Stemming from Chemical Process

Previous comparisons of simulation predictions from the CMAQ 2002 public release version showed a very large over-prediction of fine particle nitrate (less than 2.5 microns in size), to the point of being unacceptable. Comparisons against hourly data for January 2002 at the special sites of Atlanta and Pittsburgh showed huge over-predictions of nitric acid and/or total nitrate, especially at night. CMAQ includes the nighttime heterogeneous production of HNO_3 from N_2O_5 on wetted particles. The over-predictions peaked at night, suggesting an issue with this nighttime heterogeneous production of nitric acid.

The heterogeneous reaction probabilities being used in the 2002 version of CMAQ were based on Dentener and Cruzen (1993). Recent estimates of the N_2O_5 hydrolysis reaction probability are however two to three orders of magnitude smaller than those

suggested by Dentener and Cruzen (1993). The parameterization in CMAQ was updated to reflect the latest research (Riemer et al., 2003, based on experiments reported in Mentel et al., 1999), which suggested the reaction probability is much smaller, in the range of 0.02 and would be inhibited by the presence of nitrate on the aerosols, reducing it to 0.002 when nitrate is a dominant component of the mixed aerosol. In addition, the gas-phase reaction of the nitrate radical with water that produces N_2O_5 has been turned off in CMAQ. The argument is that this reaction is highly uncertain and could be a chamber wall artifact that belongs in the chamber wall model and not in the chemical mechanism. The SAPRC mechanism developer did not object to this decision, noting there was a significant degree of uncertainty about the gas-phase reaction (Carter, 2003).

A test of these new literature values for the heterogeneous reaction probabilities showed a dramatic improvement in the predictions of CMAQ for nitric acid and aerosol nitrate, although CMAQ potentially is still over-predicting nitric acid at night. Sensitivity tests with CMAQ were also conducted to further explore the degree of over-prediction in which the nighttime production of HNO_3 from N_2O_5 was turned off completely.

Figure 6 shows the monthly-averaged diurnal concentration patterns for CMAQ-predicted HNO_3 at Atlanta for (a) summer and (b) winter for the base CMAQ that includes the heterogeneous production of HNO_3 compared to CMAQ with the heterogeneous pathway completely turned off. Both model versions are compared to monthly-averaged diurnal measurements. The differences at Pittsburgh for winter (not shown) are very similar for the two CMAQ model versions compared to measurements.

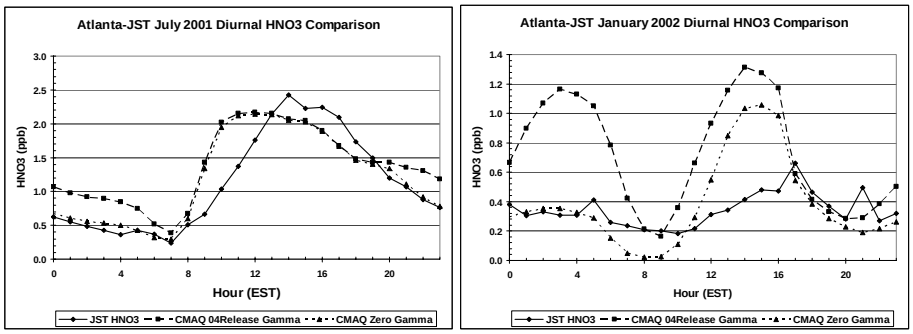

Figure 6. Comparison of the observed and predicted (base CMAQ and CMAQ with heterogeneous chemistry turned off) monthly averaged hourly diurnal pattern of HNO3 at Atlanta for (a) July 2001 and (b) January 2002.

The comparisons of the base case and sensitivity study case to the measurements show that eliminating altogether the nighttime heterogeneous production of nitric acid in CMAQ brings its predictions much more in line with the nighttime levels of nitric acid at both special sites, although now the predicted HNO_3 levels can be below the measurements. The comparisons of these CMAQ sensitivity runs show that the nighttime chemistry is most important to the overall HNO_3 budget in winter. Figure 6(b) also shows that there can be a noticeable over-prediction of nitric acid occurring in daylight hours in the winter. That is, daytime the photochemical mechanisms for ozone production (either CB4 or SAPRC99) are also contributing to the HNO_3 or total-nitrate over-prediction during the winter.

These high time resolution evaluations indicate that nighttime conversion of N_2O_5 to HNO_3 is the source of the majority of HNO_3 in winter and daytime photochemistry is the source of a majority of HNO_3 in summer. These time-resolved resolution evaluations also indicate that the heterogeneous reaction probability is still too high; thus, the "nitrate problem" has been greatly ameliorated, but not eliminated. There are suggestions in the laboratory research community and in recent ambient observations that a variety of factors exist that further inhibit these nighttime reactions, including the presence of organic aerosols or mixtures that include organics, but none are published and available for use by the CMAQ developers at this time. In addition, a wintertime issue with the photochemical production of HNO_3 has been suggested.

4. SUMMARY

There is a systematic over-prediction in the late afternoons for species that are either emitted or produced at the surface in the late afternoon and early evening. The most consistent explanation at this time is that this over-prediction is due to a premature collapse of the boundary layer in the model. For example, the late afternoon and early morning cold bias of MM5 is consistent with this explanation. The over-prediction appears to be relatively larger in urban areas and smaller in the rural areas, lending further support to the hypothesis that an important source of the problem could be the inability of the meteorological models to adequately account for the urban heat island. The degree of over-prediction also appears to be larger in summer than in winter.

Nighttime over-predictions can create compensating errors for some of the pollutants, such as EC in Atlanta (masking errors), and create systematic biases for others, such as CO, NO_Y, and summer NH_X in Atlanta (giving an incorrect sense of error). These biases also can amplify the tendency of CMAQ to over-predict fine-particle nitrate. This analysis shows that comparisons against 24-hour averages are unable to discern whether the model is getting the right answer for the right reason or for compensating wrong reason and that these comparisons form a necessary but not sufficient component of model evaluation.

The diurnal analyses together with a variety of sensitivity analyses show that the influence of the nighttime heterogeneous reactions on overall HNO_3 production is much larger in winter than in summer. In summer, the daytime, photochemical production of HNO_3 is dominant. The analysis also indicates that there can be five sources of error affecting the levels and diurnal pattern of HNO_3 concentrations: (1) error in the nighttime heterogeneous production, (2) error in the daytime photochemical production, (3) error in the NO_X emissions, (4) error in the pbl height and mixing, and (5) error in the NH_3 emissions (affecting the partitioning of total-nitrate). High time-resolution analyses of several species or species combinations besides HNO_3, including NO_Y, EC, NH_X, NH_3, SO_4^{2-}, and total-nitrate, are needed to sort out the possible sources or error and to check for compensating errors.

A serious chemical problem, relating to the heterogeneous production of HNO_3 at night in CMAQ, was, to an acceptable degree, fixed in the 2003 public release version of CMAQ with the help of these high time-resolution evaluations. They indicate, however, that the nighttime production of nitric acid in the 2003 and 2004 versions of CMAQ most

likely is still too high across much of the U.S., leading to a systematic over-prediction of total nitrate and, hence, particulate nitrate. This is corroborated by comparisons against the CASTNet data (Eder and Yu, 2004). In a relative sense the degree of over-prediction of particulate nitrate is larger in the winter, when it is more easily formed due to the lower temperatures, than in the summer. Interestingly, the two sources of bias (physical and chemical process) have roughly opposite seasonal dependencies. Thus, the seasonal balancing of surface NH_X and total-nitrate concentrations will vary across the seasons. In certain areas of the country CMAQ might be expected to predict ammonia limitation more often than it should in the colder months. Thus, CMAQ might be expected to over-emphasize the nitrate replacement (in absolute concentration terms) that can potentially offset part of the reduction in sulfate that will accompany reductions of SO_2 emissions. The hypothesis that this bias is affecting CMAQ's predicted changes of fine particles associated with emissions reductions is now being tested with further high time-resolution data coupled with model sensitivity analyses. We are continuing to investigate further both sources of bias with the intent of improving the predictions of CMAQ.

5. REFERENCES

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DISCLAIMER

The research presented here was performed under the Memorandum of Understanding between the U.S. Environmental Protection Agency (EPA) and the U.S. Department of Commerce's National Oceanic and Atmospheric Administration (NOAA) under agreement number DW13921548. Although it has been reviewed by EPA and NOAA and approved for publication, it does not necessarily reflect their policies or views.