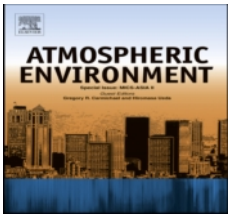

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Performance Evaluation of an Air Quality Forecast Modeling System for a Summer and Winter Season - Photochemical Oxidants and Their Precursors

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Abstract

The predictions of O_3, precursor species and the key transit species from an Air Quality Forecast Modeling System (AQFMS) are evaluated for July 2001 and January 2004 utilizing an extensive measurement data set from the PMTACS-NY "Supersite" program. The AQFMS, consisting of a chemical transport model coupled with a mesoscale meteorological forecasting model, operated routinely over the course of the six year study. The domain wide 8-hour average O_3 predictions in the summer season have an average mean normalized bias (MNB) of 8.6%. The AQFMS captured the day-to-day variations of O_3, CO, NO_x (NO_y) and SO_2 at the Queens College (urban) and Pinnacle State Park (rural) sites during both summer and winter. During July 2001, the linear regressions of CO vs. NO_x at Queens College and CO vs. NO_y at Pinnacle State Park are in reasonable agreement with observations. However, during January 2004 the slopes of the linear regressions are significantly overestimated suggesting more uncertainties with the winter emission inventories. The Ozone Production Efficiency (OPE) is under predicted by 45% at Pinnacle State Park during July 2001 which may be caused by the underestimation of NO_z removal and/or the underestimation of OH concentrations. Concentrations of HONO, a key transient specie for OH production are significantly under predicted by the AQFMS indicating deficiencies in the chemical mechanism in the AQFMS. The underestimation of OH concentrations is much more significant during January 2004 which suggests larger uncertainties with chemical mechanism for winter conditions.

Keywords:

Air quality forecast model, Ozone, Precursor gases, Hydroxyl radical, Nitrous acid

1. Introduction

Ozone and particulate matter (PM) air quality remain of great concern to the public health and regulatory communities, as these pollutants continue to show deleterious health outcomes in exposed populations, most significantly those sensitive populations at high risk (*NRC*, 1991; *Laden et al.*, 2000). The availability of a real time air quality forecast and pollution warning system capable of providing accurate air quality forecasts in a timely manner would be of significant value to the health effects, health care and regulatory communities as well as the public at large. During the past several years, there has been an increasing interest in the development and application of numerical 3-D air quality modeling systems to forecast the local or regional air quality in real time (*Cai et al.*, 2006; *McHenry et al.*, 2004; *Cope et al*., 2004; *Mckeen et al.*, 2005). The evaluation of these modeling systems has mainly focused on O_3 predictions for the summer season. However, an AQFMS must have the ability to simulate atmospheric processes/air quality throughout the year, since particulate matter, unlike O_3, is not a warm season only pollutant, but has significant contributions under cold weather conditions. The successful model must not only accurately predict ozone and particulate matter in space and time, but also their associated precursors (*Dennis et al.*, 2000). In addition, HO_x (OH and HO_2) radicals and the key chemical constituents that drive their production and termination are critical in determining the oxidative capacity of the atmosphere. Thus, the opportunity to evaluate the accuracy of predictions of the key transient species that drive atmospheric oxidation processes in model reaction mechanisms is highly desirable.

An Air Quality Forecast Modeling System (AQFMS) has been developed and operated in the Atmospheric Sciences Research Center (ASRC), State University of New York at Albany since July 2001 to evaluate the adequacy and reliability of a photochemical air quality model

system in supporting real-time 24-hr air quality forecasts for ozone, $PM_{2.5}$ and the precursors for the Northeastern United States. In this paper, the predictions of gaseous species including O_3 and precursor species (CO, NO_x/NO_y, SO_2, VOC) as well as two key transient species: HONO and HO_x radical for a summer (July 2001) and a winter month (January 2004) are evaluated. During these two months, intensive field campaigns of $PM_{2.5}$ Technology Assessment and Characterization Study-New York (PMTACS-NY), one of EPA's Supersite programs (*Solomon and Hopke*, 2008), were conducted at Queens College, New York City. A variety of measurements utilizing advanced instrument technologies performed during the two campaigns provide a detailed chemical characterization of the gas and particle phase composition of the atmosphere (*Drewnick et al*., 2004; *Ren et al.*, 2003; 2006; *Weimer et al.,* 2006) and provide a unique opportunity to evaluate the performance of modeling systems like the AQFMS. Measurements of O_3, CO, SO_2, NO_x and NO_y performed at Pinnacle State Park in Addison, NY, a regional/rural site located in the southern tier along the New York - Pennsylvania border, are also used in the model evaluations, providing a unique opportunity to compare and contrast urban-rural and seasonal differences. The availability of HO_x (OH and HO_2) and nitrous acid (HONO) measurements also provide a unique opportunity to evaluate the chemical mechanism within the AQFMS and identify sources of model uncertainty.

2. Operational AQFMS

The three core models in the AQFMS are the SKIRON/Eta meteorology model, the Sparse Matrix Operator Kernel Emissions (SMOKE) processing system and the Comprehensive Air Quality Model with Extensions (CAMx). The ETA model which is fully operational in the National Weather Service providing weather forecasting in United States (*Black*, 1994) has been

1 further developed at the University of Athens for project SKIRON (*Kallos et al.*, 1997). The
2 statistical assessment of SKIRON/Eta for a 12-month period show satisfactory predictions of
3 wind speed/direction, air temperature and mean sea surface pressure (*Papadopoulos et al.*, 2001).
4 The AQFMS used SMOKE processed emissions from the National Emission Inventory 1999
5 (NEI99), the most up-to-date inventory at the time of this application. Biogenic emissions are
6 estimated by the Biogenic Emission Inventory System (BEIS2) module incorporated in SMOKE
7 and are affected by both temperature and radiation. It should be noted that differences between
8 1999 and 2001 emissions are not expected to be significant, as major emission changes with
9 respect to the NO_x SIP Call (*USEPA,*1998) did not get underway until 2002. In addition, as
10 pointed out in *Frost et al.* (2006), winter emissions are not significantly affected by the NO_x SIP
11 Call which is geared to address summertime emissions impacting ozone exceedences and thus,
12 not likely to introduce significant changes to 2004 winter emission. The Comprehensive Air
13 Quality Model with Extensions (CAMx) version 4.0 (*Environ*, 2003) used in the AQFMS, is a
14 "state of the science" Eulerian photochemical grid model that allows for integrated assessment of
15 gaseous and particulate air-pollution with many notable features. In the operational air quality
16 forecast, the CBM4 mechanism with revised radical-radical termination reactions and updated
17 isoprene chemistry based on (*Carter*, 1996) is used for gas phase chemistry. Aqueous phase
18 chemistry follows the approach developed for RADM (*Chang et al.*, 1987)

19 The domains of SKIRON/Eta and CAMx are illustrated in Figure 1. Nested grids are
20 used in the CAMx model in order to provide air quality forecasts at finer resolution in the region
21 of greatest interest (in this case, the northeastern USA) while simulating the regional air masses
22 outside this domain at coarser resolution. The coarse CAMx domain covers the area from (26°N,
23 99.0°W) to (47°N, 67°W) with 1/2 deg longitude by 1/3 deg latitude horizontal grid (roughly 36

km) increment and the number of grid points x-y plane is 64 x 63. The fine CAMx domain covers the area from (31.9°N, 92.2°W) to (44.1°N, 69.3°W) with 1/6 deg longitude by 1/9 deg latitude (roughly 12 km) horizontal grid increment and the number of grid points x-y plane is 137 x 110. There are 14 vertical model layers for both fine and coarse domains extending from the surface to about 4000 m aloft. A time-invariant boundary condition with ozone background concentration at 35 ppb was prescribed for the CAMx coarse domain for all the heights. The nested grid allows the fine domain to use the predicted pollutant concentrations from coarse domain as the boundary condition, reducing the impact of the artificial boundary condition set for the coarse domain. 35 ppb of O_3 is also used as the top boundary of the entire model grid. The contribution of the free tropospheric O_3 above 4000 m is treated as an upper boundary condition in the model. While the recently released ozonesonde data (http://croc.gsfc.nasa.gov/intexb/ions06.html) show that ozone at 4 km is more in the range of 50-70 ppb over northeastern U.S, our sensitivity studies indicate less than a 5% increase in surface layer O_3 concentrations with the application of 60 ppb as the top boundary condition. Since PBL heights > 4 km are rare in the northeast, this also suggests that the exchange between free troposphere and boundary layer does not significantly impact the forecast for surface level for our study time periods. The left lower and right upper corners of the SKIRON/Eta domain are located at (23.6°N, 106.7°W) and (50.4°N, 59.5°W) respectively. The horizontal grid increment is 0.12 x 0.12 deg and there are 32 vertical layers with the top layer at 15.8 km. The meteorological parameters generated by SKIRON/Eta are interpolated to the coarse and fine CAMx grids before they are applied as the input for CAMx. Initial conditions for the CAMx air quality simulation are obtained from the previous day's forecast. If the previous day's forecast is not available, a two-day spin-up simulation starting from nominal initial conditions is performed

prior to the forecast simulation. These include initial and boundary conditions of 35 ppb for ozone and based on the analyses of CO measurements at multiple rural sites, 100 ppb and 180 ppb as boundary and initial condition for CO during summer and winter respectively. The forecast results presented in this paper are all from the fine domain simulation.

3. Observation Data

The evaluation analyses for the domain-wide predictions of ozone during summer month draw upon the observations from EPA's AQS. These data are available online from (*http://www.epa.gov/ttn/airs/airsaqs/detaildata/downloadaqsdata.htm*). Detailed air quality observations from the two PMTACS-NY Supersite monitoring sites located at Queens College in Queens, NY (urban, 40.7°N, 74.0°W) and Pinnacle State Park in Addison, NY (rural, 42.1°N, 72.2°W) are used to assess the model's capabilities in capturing urban and rural air mass characteristics over different seasons. The locations of the two sites are shown in Figure 1. In addition to routine air quality parameters (SO_2, NO, NO_2, O_3, CO, NMHC), transient species (e.g., HO_x(OH, HO_2) and HONO) were also measured during PMTACS-NY Queens College July 2001 and January/February 2004 field intensive. This compliment of data is used to evaluate the overall performance of the AQFMS and most uniquely its ability to predict radical chain lengths and the oxidative capacity of the sampled air masses, both critical in understanding the production of secondary pollutants.

4. Meteorology Forecasts

Meteorological inputs are essential to air quality modeling and the accuracy of meteorological forecasts will largely affect the accuracy of air quality prediction (*Seaman*, 2000).

It should be noted that regulatory applications of air quality simulation models are performed using meteorological hindcast data with observational data assimilation. Such applications should under most circumstances produce more accurate meteorological input parameters than that associated with real-time unperturbed meteorological forecasts, which do not have the benefit of such data nudging and therefore face a great challenge in forecasting air quality concentration fields. Mean Bias Error (MBE) $\overline{a_{\mathrm{mod}}(x,t) - a_{obs}(x,t)}$ (*Hogrefe et al.*, 2001) for SKIRON/Eta predictions of temperature at a height of 2 meters and wind speed at a height of 10 meters are calculated using the observation data for measurement sites within the fine modeling domain. The data are retrieved from the Data Support Section at the National Center for Atmospheric Research (NCAR-DSS). For July 2001, SKIRON/Eta has an average positive bias of 0.97 ºC for 2 m temperature and a positive bias of 0.48 m/s for 10m wind speed prediction. For January 2004, SKIRON/Eta has a negative bias of -1.31 ºC for 2 m temperature and a positive bias of 1.2 m/s for 10 m wind speed. These values are comparable with those from MM5 and RAMS3b predictions (*Hogrefe et al.*, 2001) showing similar levels of performance between the respective models. We also provide the time series and diurnal comparisons for relative humidity and temperature at Queens College for July 2001 and January 2004 in Figure 2. The comparisons consider the post-processed predictions as inputs for the first model layer of CAMx (the middle of the first layer is 25 m) with the surface measurements. The July 2001 time series data indicate that the SKIRON/Eta performs reasonably well in predicting RH and temperature. There is slight systematic under prediction of temperature and over prediction of RH for both seasons. The biases may be partly due to the fact that the model grid containing the Queens College monitor site is adjacent to water and the grid resolution does not fully capture the sea-land interaction.

5. Air Quality Forecast Results

5.1 Statistical Evaluation for Domain Wide O_3 during Summer

One of the principal goals of this AQFMS is to alert the public of impending unhealthful O_3 and $PM_{2.5}$ air quality. Figure 3 shows a map of the calculated mean normalized bias (MNB) of daily maximum 8-hour average ozone predictions during July 2001. $MNB = \frac{1}{n}\sum_{i=1}^{n}\left(\frac{(Model_i - Obs_i)}{Obs_i}\right)\times 100\%$ is computed using the observations from EPA's AQS database at 574 monitoring stations within the fine domain. The MNB calculated with a cutoff value of 60 ppb applied to the observations is recommended by the EPA for the assessment of ozone predictions for the concentrations at or above the 8-hour standard of 85 ppb (*USEPA, 2005*). Figure 3 shows that the MNB typically range from -15% to 25% for the whole domain with model over prediction greater than 35% present for some sites along the Ohio Valley region and eastern Kentucky and Alabama. The over predictions within these regions are consistent with the findings from *McKeen et al.* (2005). The MNBs for urban sites in the northeastern corridor are mostly in the +5% to -15% range consistent with U.S. EPA performance objectives for episodic days.

5.2 Predicted and Observed Hourly Concentrations for Gaseous Species at Queens College (urban) and Pinnacle State Park (rural) during July 2001 and January 2004

5.2.1 Summer Evaluation Results

Figure 4 shows hourly time series of model predictions and observations for O_3, CO, NO_x, SO_2 and total non-methane hydrocarbon (NMHC) at Queens College during 14-31 July 2001 (all days begin at 0:00am EST). The AQFMS predicted O_3 concentrations show very consistent day-to-day and diurnal variations with the observations. The predicted CO, NO_x, SO_2

and NMHC concentrations match the observations well for the entire time period of July 2001, with the exception that the model missed the high CO, NO_x and NMHC concentration events which took place during the nights of 20-21 and 30-31 July. Both the observations and predictions show strong correlation between CO and NO_x, while the correlation between NO_x and SO_2 are much less significant. Northerly winds during these nights indicate that the site was impacted by mobile source emissions from the Long Island Expressway a few hundred meters to the north. It is also evident that there is a build up of O_3 from 14 to 17 July which is consistent with the build up of the temperature. The low O_3 concentrations on the 14 July correspond to the post-passage of a cold front from the north which swept the polluted air mass to southeast and finally to the ocean. From 16th, a subtropical high pressure system started to build up over most part of the eastern US and persist during the following day. A strong southwesterly flow brought an O_3 rich air mass from Ohio Valley and southeast region to the northeast. As indicated in Figure 3, the positive biases of O_3 are mostly found in the Ohio Valley, so the over predictions of O_3 at Queens College during 16-17 July are likely influenced by the O_3 over predictions in these upwind regions. These over predictions do not show up at Pinnacle State Park on 16 July (Figure 5) since the site was still under the impact of northerly flow during the day. The enhancements in precursor species during 16-17 July are also evident and successfully captured by the AQFMS with some biases. The spatial distribution maps suggest that the enhancement of SO_2 is due to the transport from Ohio Valley while the enhancements of CO, NO_x and NMHC are more likely from the lower part of the northeastern urban corridor.

The observed and predicted hourly time series of O_3, CO, NO_x, and SO_2 at Pinnacle State Park during July 2001 are shown in Figure 5. The measurements for total nitrogen, denoted as NO_y ($NO_y = NO_x+HNO_3+HONO+NO_3+N_2O_5+RNO_3$) and HNO_3 are also available for this

rural site providing opportunity to track the model prediction of the total nitrogen budget of aged air masses as well. NO_y is conserved in terms of chemical transformations, but can be depleted by physical removal processes (*Parrish et al.*, 1991). HNO_3 is typically a major component of the NO_y budget and the reaction of $OH+NO_2$ to form HNO_3 is the dominant sink for OH in polluted atmospheres. It is shown in Figure 5 that the predicted concentrations for O_3, CO, NO_y, NO_x, SO_2 and HNO_3 at Pinnacle State Park all track the temporal variations of the observations well. Elevated NO_x concentrations observed during many nighttime periods over the July period suggest the presence of elevated plumes, likely trapped in stable layers, entraining on the monitoring site. The treatment of the nocturnal boundary layers being a well known shortcoming on mesoscale meteorological models. Enhanced HNO_3 concentrations as well as low NO_x/NO_y ratios, when HNO_3 measurements are not available, are suggestive of aged air masses that have not encountered precipitation. The O_3 over predictions during 17-18 July are associated with the over predictions of NO_y, HNO_3 and SO_2. With its long life time (~2-3 months), CO can serve as a good indicator for transport. The CO predictions are in excellent agreement with the observations during the entire time period including 17 and 18 July indicating that transport from upwind urban centers is adequately predicted by the model. The over predictions of SO_2 and NO_y, are likely due to point source emissions in the upwind regions and/or potential uncertainties with the aqueous phase chemistry in the model since both SKIRON/Eta and measurement show the existence of cloud over Pinnacle State Park during the two days. Our calculation shows that the mean NO_z/NO_y ratio (an indicator for the age of the air mass) from AQFMS is 0.75, slightly higher than the ratio of 0.60 from the observations.

5.2.2 Winter Evaluation Results

Time series data for O_3 and precursor gas measurements and predictions for Queens College during the time period from 8-31 January, 2004 are shown in Figure 6. NMHC measurement data are not available for this time period, but CO can serve as a reasonable surrogate for this component. As expected, O_3 concentrations in winter are much lower than in summer at both sites due mainly to reduced solar insolation and its impact on photochemical activity. Winter predictions and observations show a general increase in concentrations compared to summer of 40% and 25% on average for NO_x and 20% and 10% on average for CO respectively, while SO_2 concentrations were 50% and 100% higher on average. These findings are consistent with the lower PBL heights and increased wintertime emissions of the respective species. At Queens College the O_3 concentrations vary from zero to ~30ppb. Though O_3 data are missing during the hours when peak NO_x concentration are observed during 12, 17 January, low O_3 concentrations are observed during 22, 28 January 2004 with correspondingly high concentrations of NO_x indicating strong titration events. The temporal characteristics of these events are captured by the AQFMS. The CO predictions are generally biased high during midday and in better agreement with observations during nighttime hours. NO_x concentrations are under predicted for most days, in contrast to the CO predictions, but are in better agreement with observations for the daytime hours than nighttime hours. The predicted SO_2 concentrations overall show good agreement with observations during this winter month, with some plume structure missed by the model, typically during nighttime hours. The three episodes at Queens College during the periods of 11-13 January, 17-18 January and 21-22 January, each features high concentrations of CO, NO_x and SO_2 from both observations and predictions, all correspond to air mass changes associated with relatively high temperature and relative humidity (Figure 2).

The time series of predicted and observed gas species at Pinnacle State Park during January 2004 presented in Figure 7 show strong ozone depletion events associated with increased concentrations in CO, NO_x and SO_2 on 12, 18, 22, 24, and 28 January, features well captured in the model predictions. For the days when O_3 concentrations are not perturbed by the fresh polluted air, predicted and observed O_3 concentrations at Pinnacle State Park are about 35 ppb, a value associated with regional background. NO_y is under predicted for most of the days and consistent with the under prediction of NO_x, though the under prediction is counteracted partly by the over prediction of HNO_3 which is possibly due to the too active NO_x transformation processes and/or the low removal process in the model. The average ratio of NO_z/NO_y is 0.68 and 0.30 from prediction and observation respectively suggesting the air mass is more aged in the model. SO_2 predictions show good agreement with observations for the entire period with the exception of the last few hours of 21 January and early morning of 22 January when the model under predicted high SO_2 observed concentrations (up to 30 ppb) and NO_y concentrations. The event is likely the result of a point source plume impacting the monitoring site that was missed by the model due to errors in transport or limited grid resolution.

5.3 Correlations of Gaseous Species

Emission sources of CO and NO_x are dominated by anthropogenic activities. Comparisons of predicted and observed correlations of NO_x (or NO_y) and CO provides an indication of the basic performance of the model, the quality of the emission inventory and precursor chemistry (*Cardenas et al.*, 1998; *Parrish et al.*, 1991). Queens College, a site strongly impacted by the fresh emissions as evidenced by night plumes from the Long Island Expressway (e.g. July 21 and July31) and diurnal traffic emissions patterns in CO and NO_x observations, is

contrasted with Pinnacle State Park, a site typically influenced by more aged air masses. Pinnacle State Park measurements provide another useful indicator for assessing regional photochemistry through the correlation of O_3 and NO_z (NO_y–NO_x). The slope of the linear portion of the O_3 vs. NO_z correlation is defined as the O_3 production efficiency (OPE), a measure of the number of O_3 molecules produced per NO_x molecule consumed (*Trainer et al.*, 1993). Such comparisons provide basic understanding of the model's performance relative to the O_3 - NO_x-VOC precursor relationship, which is of fundamental importance in air quality management. Linear regression of O_3 vs. NO_z concentrations at Pinnacle State Park considered measurements during the daytime hours from 9:00am to 5:00pm when the boundary layer is well developed (*Trainer et al.*, 1993) for both July 2001 and January 2004. It should be noted that other indicators of precursor relationships have been suggested (*Sillman*, 1995; *Sillman and He,*2002; *Tonnesen and Dennis* 2000), but most are limited by the availability of measurement data.

5.3.1 Summer Correlations

The linear regression of observed and predicted CO vs. NO_x at Queens College shown in Figure 8 for July 2001 has an intercept of 141 ppb and a slope of 7.7 with R^2 equal 0.79 from observations and an intercept of 189 ppb and a slope of 10.4 with R^2 equal 0.87 based on model predictions, suggesting a strong correlation between these precursor species. Since the Queens College measurement site is located in the vicinity of two major highways (≤ 1 km) and predicted CO and NO_x concentrations are averaged over the 12 km grid element, the higher slope of CO vs. NO_x from model predictions is consistent with NO_x's relatively shorter lifetime compared to that of CO. The AQFMS also accurately predicts the NMHC/NO_x ratio which plays key role in NO_x-VOC-O_3 relationship and O_3 formation (*NARSTO*, 2000). The linear regression

of NMHC vs. NO_x model predictions has an intercept of 23 ppbC and a slope of 2.8 with an R^2=0.81, both the intercept and slope are consistent with the observed linear regression having an intercept of 35 ppbC, a slope of 2.6 with an R^2=0.6.

At Pinnacle State Park, the forecasted CO vs. NO_y linear regression has a slope of 13.9 and an intercept of 89 ppb, in very good agreement with observations which have a slope of 14.0 and intercept of 104 ppb. These results suggest that the model performs well in capturing the characteristics of the regional precursor emissions, transformation and transport. The R^2 for the linear regression of predictions is 0.80 and that for observations, 0.48, suggest much greater variability in the observations due to temporal and spatial smoothing in the model as a result of the 12 km grid resolution of the model. The results reported for the O_3 vs. NO_z linear regression at Pinnacle State Park indicate a model-predicted slope of 4.8 (R^2=0.94), about 55% of the observed slope of 8.9 (R^2=0.75). Possible explanations for the difference in OPE include: 1) the overall reactivity of the emissions is underestimated, 2) the removal process of NO_z species may be underestimated by the AQFMS, 3) plumes are diluted, leading to more efficient NO_z production, or 4) the chemical mechanism in the model does not adequately captured the photochemical cycles associated with ozone production. The latter explanation is further investigated in the later section.

5.3.2 Winter Correlations

During the winter month of January 2004, the linear regression analysis of observed CO vs. NO_x at Queens College indicates a slope of 4.2 with R^2=0.48, much lower than prediction data which reports a slope of 11.7 and R^2=0.95 (see Figure 8, right column). Given the low photochemical reactivity during the winter season, the observed CO vs. NO_x slope at this site

should mostly reflect the emission ratio from mobile sources. In fact, this ratio is consistent with measurements from a roadside site in New York City (PS-59) which report a CO vs. NO_x slope of 4.7 for the same period of time. The discrepancy between the predicted and the observed slopes suggest that NEI99 mobile emission inventories remain significantly uncertain at this particular urban site. The intercepts for the linear regressions are 200 ppb and 263 ppb for observation and prediction respectively, and are higher than those in July 2001 campaign. These differences reflect the general increase in the winter CO background concentration resulting from its increased chemical lifetime, increased emissions and lower mixing layer heights.

At Pinnacle State Park in January 2004, the linear regression of predicted CO vs. NO_y has a slope of 21.5 and an intercept of 188 ppb while the slope for the observation data is 6.9 with an intercept of 185 ppb. The over prediction of the slope of CO vs. NO_y reflects the overall under prediction on NO_x during winter month, and also partly caused by the under prediction of NO_y for the events when the measurement site is mostly likely under impact of point source plume. This is consistent with the over prediction of the slope of CO vs. NO_x correlation at Queens College during the same month. For winter O_3 vs. NO_z linear regression, the AQFMS predicted data show a slope of -2.2 and an intercept of 33 ppb very close to the values from the observation data which show a slope of -2.4 and an intercept of 32.6 ppb. However, the R^2 of the regression between O_3 and NO_z from both the observations and predictions are only about 0.1. O_3 concentrations in winter season are dominated by the background O_3 boundary condition with little O_3 production from local photochemistry. The negative slopes with low correlation coefficients for observations and predictions at Pinnacle State Park during January 2004 suggest that the variation of O_3 during winter is mainly due to titration from NO emissions in the region.

It is interesting that winter regression slopes of CO vs. NO_x observations at Queens College and CO vs. NO_y at Pinnacle State Park are both about half the summer slopes while the predicted data show higher winter slopes than summer slopes. The higher predicted winter slopes are consistent with the higher winter mole emission ratio from the inventory. (i.e. average emission ratio for the 9 grids centered at Queens College is 8.4 in winter and 7.2 in summer). The discrepancies between the model prediction and the observation suggest larger uncertainties in the winter emission inventory.

5.4 Predicted and Observed Hourly Concentrations of HO_x Radicals and HONO at Queens College during July 2001 and January 2004

5.4.1 HO_x Comparison

The OPE is closely tied to the model's ability to capture the chain length of atmospheric photochemical oxidation cycles. Hydroxyl radical (OH) and HO_x chemistry overall are key to understanding the photochemical oxidation capacity of the troposphere. The OH radical initiates oxidation processes of most atmospheric trace gases especially NMHC and regulates the net chemical production of ozone (*Poppe et al.*, 1994).

In the air quality forecast modeling system, the chemical mechanism must accurately reproduce radical processes and related precursor and product concentration relationships, if it is to have creditability as an air quality management tool for regulatory guidance. OH and HO_2 radical concentrations measured by a laser-induced fluorescence instrument during the PMTACS-NY intensive campaign in Queens College in July 2001 and January 2004 (*Ren et al.*, 2003; 2006), provide unique information in the evaluation of the performance of AQFMS especially as it relates to the simulation of the oxidative capacity of the atmosphere.

The time series data and diurnal patterns of predicted and observed OH concentrations at Queens College for the period from 14 to 31 July are illustrated in Figure 9. For the 18 days, both the predicted and observed OH concentrations vary mostly from ~ 0 to 0.5 ppt. The predicted OH concentrations show reasonable agreement with observations and indicate a moderate bias for under prediction with the exception of 25 July 2001. During 18 July when the largest discrepancies between prediction and observation occur, the observed solar radiation at Queens College on that day shows the pattern of clear sky, while the modeled actinic flux reflects significant attenuation from an incorrect prediction of cloud cover over the Queens College area. The general tendency of OH under prediction for this summer month is also evident in the diurnal plot. The diurnal patterns shown in Figure 9 are the means of the days from 14 to 31 July. The observations show that OH peaks at 14:00 EST while the predicted data show daily maximum OH concentration at 13:00 EST. The average predicted OH concentrations are about 0.05 ppt lower than the observed OH concentrations for all hours. The observations also show that OH concentrations are sustained at a relatively high level of about 0.05 ppt during night while the predicted OH concentrations approach zero.

The time series and diurnal patterns of predicted and observed OH concentrations at Queens College for the period from 14 to 31 January 2004 are illustrated in Figure 10. During the 18 days, the observed OH concentrations vary from ~0 to 0.09 ppt, about 1/5 of those for the summer month. The observed OH concentrations are significantly underestimated by AQFMS for this winter month with the predicted concentrations varying from 0 to 0.018ppt. The OH concentration reaches maximum between 12:00-13:00 EST for the winter month from both observation and prediction. The HO_2 prediction (not shown here) also biased low to a significant

degree during day time in both summer and winter which is very consistent with the OH prediction.

5.4.2 HONO Comparison

It is evident that the OH concentrations are under predicted in AQFMS at Queens College for both summer and winter season with more significant underestimation in winter. The discrepancies in OH predictions versus observations raise concerns regarding the radical production and loss in the chemical model used in the AQFMS. The initial sources of OH radical include the photolysis of ozone followed by the reaction of electronically excited $O(^1D)$ with H_2O; photolysis of nitrous acid; and the reaction of alkenes with ozone. Many studies (*Martinez et al.*, 2003; *Tan et al.*, 2001) have found that the formation of $O(^1D)$ from the photolysis of O_3 and its subsequent reaction with water $O(^1D)+H_2O\rightarrow 2OH$ dominates the new OH production in the late morning and afternoon. *Ren et al.* (2003) use measured concentrations of precursor species and meteorology data collected at July 2001 Queens College field campaign as input to a box model. The budget studies from their box model indicate that apart from $HO_2+NO\rightarrow OH+NO_2$, the most important OH source is daytime photolysis of HONO for the Queens College during July 10 to Aug 2, 2001. The production and loss rates from the AQFMS are derived from the predicted precursor concentrations, which are emission inventory based, and their reaction products. Thus, any bias in the predictions of the precursor species or products, e.g. HONO, will certainly cause a bias in the prediction of OH.

The comparisons of observed and predicted HONO at Queens College for the period of 19-28 July 2001 and 17-31 January 2004 are provided in Figure 11. During the 10 days in July 2001, the observed HONO concentrations vary from 0.17 ppb to 4.1 ppb with a mean

concentration of 0.8 ppb, the highest HONO concentration of 4.1 ppb was observed during the early morning of July 21. The predicted HONO concentrations from the AQFMS range from 0 ppb to 0.19 ppb for this study period, with a mean concentration of 0.035 ppb. During the 15 winter days, the observed HONO concentrations vary from 0.16ppb to 1.76ppb with a mean concentration of 0.55 ppb. The predicted HONO concentrations range from 0 to 0.04 ppb for the winter study period, with a mean concentration of 0.007 ppb. The model predicted HONO concentrations are systematically under predicted suggesting that the CBM4 chemical mechanism has chemical deficiencies and is not capturing the full extent of the chemistry of HONO in the atmosphere. In another paper (*Cai et al*., 2008, to be submitted), HONO formation mechanisms associated with heterogeneous surface based reactions added to the standard CBM4 mechanism in CAMx lead to significant improvements in the prediction of HONO and OH radical concentrations. These improvements in predictions, in turn, increase the model predicted OPE, bring it closer to observation. These results suggest that the model projected ozone attainment strategies may have significantly uncertainties as a result of deficiencies in model's chemical mechanism.

The larger discrepancies of OH predictions in winter than in summer also suggest that there may be more uncertainties in chemical mechanism under winter conditions. It is worth noting that the chemical mechanisms used in all chemical transport models have been developed under conditions associated with high photochemical oxidation (i.e. typical summertime solar and temperature conditions), therefore it is not particularly surprising that they may not capture the details of chemical transformations under low light, low temperature conditions. Although these winter time condition are not conducive to high ozone production events, winter time OH plays an important role in secondary production of PM and therefore must be predicted with

improved accuracy, to assure the credible application of air quality models to the development of mitigation strategies for the attainment of PM2.5 National Ambient Air Quality Standard.

6. Summary

The predictions of O_3 and related precursor species and key transient species from an AQFMS are evaluated for a summer and winter month, July 2001 and January 2004 respectively. The overall mean normalized bias (MNB) for daily maximum 8-hour average ozone concentrations higher than 60 ppb for the model domain during the summer month of July 2001 is 8.6%. The AQFMS successfully captured the temporal patterns of O_3, CO, NO_x, SO_2 at the urban site (Queens College, NY) and O_3, CO, NO_y, SO_2 at the rural site (Pinnacle State Park, NY) for both summer month and winter month. The AQFMS captures the temporal variations of these species for both the two month. However, the AQFMS does not fully capture the variations of precursor species at Queens College when this urban site was impacted by local mobile emission and at Pinnacle State Park when the site was impacted by plumes from point sources.

The linear regression of model-predicted CO vs. NO_x at Queens College and CO vs. NO_y at Pinnacle State Park during July 2001 are very comparable with those derived from observations indicating that the emissions of precursor species as well as transport are well simulated in the model during the summer season. However the predicted O_3 production efficiency (OPE) at Pinnacle State Park is only 55% of that from observation which suggests that the removal process of NO_z species during transport might be underestimated by the model and/or the chemical mechanisms in the model does not adequately capture the photochemical cycles associated with ozone production. Analysis of Queens College data suggests that OH concentration a key indicator of the oxidative capacity of an air mass, is generally under

predicted in the model and the under prediction of HONO concentrations is likely a significant contributing factor to OH under prediction. Ongoing studies suggest the need to revisit primary HONO emissions and chemistry in the model. Measurement of a more complete set of species to be able to reconstruct NO_y from the ground up are also necessary to better address the OPE discrepancy. The CO/NO_x ratio at Queens College and CO/NO_y ratio at Pinnacle State Park are significantly overestimated during winter season. The discrepancies between the observed and predicted ratios might reflect more emission uncertainties during the winter season. Also, the OH concentrations are significantly underestimated during January 2004 suggesting more uncertainties with the chemical mechanism in capturing the details of chemical transformations under low light, low temperature conditions.

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References:

Black, T. L. (1994), The new NMC mesoscale eta model: Description and forecast examples, *Wea. Forecasting*, *9*, 265-278.

Cai, C. (2006), Implementation and performance evaluation of an air quality forecast modeling system (AQFMS) for northeastern USA, Ph.D dissertation, State University of New York at Albany, Albany, New York.

Cai, C et al. (2008), Performance Evaluation of an Air Quality Forecast Modeling System for a Summer and Winter Season - HONO Formation Processes and Their Implications for HO_x Budgets, to be submitted to *Geophys. Res. Lett*

Chang, J. S., R. A. Brost, I. S. A. Isaksen, S. madronich, P. Middleton, W. R. Stockwell and C. J. Walcek (1987), A Three-dimensional Eulerian Acid Deposition Model: Physical Concepts and Formulation. *J. Geophys. Res*., 92, 14,681-14700.

Cardenas, L. M., J. F Austin, R. A. Burgess, K. C. Clemitshas, S. Dorling, S. A. Penkett and R. M. Harrison (1998), Correlations between CO, NO_y, O_3 and non-methane hydrocarbons and their relationships with meteorology during winter 1993 on the north Norfolk coast, U.K., *Atmos. Environ.*, *32*(19), 3339–3351.

Carter, W. P. L. (1996), Condensed atmospheric photooxidation mechanisms for isoprene. *Atmos. Environ.*, *30*, 4275-4290.

Cope, M. E., G. D. Hess, S. Lee, K. Tory, M. Azzi, J. Carras, W. Lilley, P. C. Mannis, P., Nelson, L. Ng, N. Wong, S. Walsh and M. Yong (2004), The Australia air quality forecasting system. Part I: Project description and early outcomes, *J. Appl. Meteo.*, *43*, 649-662.

Dennis, R. L., J. R. Arnold, and G. S. Tonnesen (2000), On the need for better ambient observations of important chemical species or air quality model evaluation. In: McClenny, W.

A. (Ed.), Recommended Methods for Ambient Air Monitoring of NO, NO_2, NO_y, and Individual NO_z species, EPA Report No. EPA-600/R-01/005, Office of Research and Development, Research Triangle Park (Chapter 4).

Drewnick, F., J. J. Schwab, J. T. Jane, M. Canagranta, D. R. Worsnop, and K. L. Demerjian (2004), Measurement of ambient aerosol composition during the PMTACS-NY 2001 using and aerosol mass spectrometer. Part II: chemically speciated mass distributioins, *Aerosol Sci. and Technol.*, *38*, 104-207.

Environ (2003), User's Guide Comprehensive Air Quality Model With Extensions (CAMx) Version 4.00.

Frost, G. J., et al. (2006), Effects of changing power plant NOx emissions on ozone in the eastern United States: Proof of concept, J. Geophys. Res., 111, D12306, doi:10.1029/2005JD006354.

Hogrefe, C., S. T. Rao, P. Kasibhatla, W. Hao, G. Sistla, R. Mathur, and J. McHenry (2001), Evaluating the Performance of Regional-Scale Photochemical Modeling Systems: Part I - meteorological predictions, *Atmos. Environ.*, *35*, 4159-4174.

Kallos, G., S. et al., (1997), The Regional Weather Forecasting System SKIRON and its capability for forecasting dust uptake and transport. Proc. Of the WMO conference on dust storms, 6 November 1997, Damascus, Syria.

Laden, F., L. M. Neas, D. W. Dockery, and J. Schwartz (2000), Association of fine particulate matter from different sources with daily mortality in six US cities, *Environ. Health Perspect.*, *108*, 941-946.

Martinez, M., et al. (2003), OH and HO_2 concentrations, sources, and loss rates during the Southern Oxidants Study in Nashville, Tennessee, summer 1999, *J. Geophys. Res.*, *108*, 4617, doi: 10.1029/2003JD003551.

McHenry, J. N., W. F. Ryan, L. S. Nelson, J. C. Carlie Jr., J. Pudykievicz, S. Arunachalam and J. M. Vukovich (2004), A real-time Eulerian photochemical model forecast system Overview and initial ozone forecast performance in the Northeast U.S. Corridor, *Bull. Amer. Meteor. Soc.*, 525-548.

McKeen, S., et al. (2005), Assessment of an ensemble of seven real-time ozone forecasts over eastern North America during the summer of 2004, *J. Geophys. Res.*, *110*, D21307, doi:10.1029/2005JD005858.

NARSTO (2000), An assessment of tropospheric ozone pollution: a North American perspective, available at http://www.narsto.com.

National Research Council (1991), Rethinking the Ozone problem in Urban and Regional Air Pollution, National Academy Press, Washington, District of Columbia.

Parrish, D. D., M. Trainer, M. P. Buhr, B. A. Watkins, and F. C. Fehsenfeld (1991), Carbon monoxide concentrations and their relation to concentrations of total reactive oxidized nitrogen at two rural U. S. sites, *J. Geophys. Res.*, *96*, 9309-9320.

Poppe, D., et al., (1994), Comparison of measured OH concentrations with model calculations, *J. Geophys. Res.*, *99*, 16,633-16,642.

Ren, X, W. H. Brune, J. Mao, M. J. Mitchell, R. L. Lesher, J. B. Simpas, A. R. Metcalf, J. J. Schawab, C. Cai, Y. Li, K. L. Demerjian, H. D. Felton, G. Boynton, A. Adams, J. Perry, Y. He, X. Zhou, J. Hou (2006), Behavior of OH and HO_2 in the Winter Atmosphere in New York City, *Atmos. Environ.*, 40, S252-S263

Ren, X, H. Harder, M. Martinez, R. L. Lesher, A. Oliger, T. Shirley, J. Adams, J. B. Simpas, W. H. Brune (2003), HOx concentrations and OH reactivity observations in New York City during PMTACS-NY2001, *Atmos. Environ.*, 37,.3627-3637.

Seaman, N. L. (2000), Meteorological modeling for air quality assessments. NARSTO Critical Review Papers Special Issue, *Atmos. Environ.*, *34*, 2231-2260.

Sillman, S and D. He (2002), Some theoretical results concerning O_3-NO_x-VOC chemistry and NO_x-VOC indicators, *J. Geophys. Res.*, *107*(D22), 4659, doi:10.1029/2001JD001123.

Sillman, S. (1995), The use of NO_y, H_2O_2, and HNO_3 as indicators for ozone-NO_x-hydrocarbon sensitivity in urban locations, *J. Geophys. Res., 100*, 14,175–14,188.

Solomon and Hopke (2008), Special Issue of *JA&WMA* Supporting Key Scientific and Policy- and Health-Relevant Findings from EPA's Particulate Matter Supersites Program and Related Studies: An Integration and Synthesis of Results, *J. Air & Waste Manage. Assoc.* **58**:137–139.

Tan, D., et al. (2001), HO_x budget in a deciduous forest: Results from the PROPHET summer 1998 campaign, *J. Geophys. Res.*, *106*, 24,407–24,427.

Tonnesen, G. S and R. L. Dennis (2000), Analysis of radical propagation efficiency to assess ozone sensitivity to hydrocarbons and Nox 2. Long-lived species as indicators of ozone concentration sensitivity, *J. Geophys. Res.*, *105*, 9227-9241.

Trainer, M., et al., (1993), Correlation of ozone with NO_y in photochemically aged air, *J. Geophys. Res.*, *98*, 2917-2925.

U.S. Environmental Protection Agency (1998), Finding of Significant Contribution and Rulemaking for Certain States in the Ozone Transport Assessment Group Region for Purposes of Reducing Regional Transport of Ozone, Federal Register, Vol. 63, No. 207, 1998.

U.S. Environmental Protection Agency (2005), Guidance on the Use of Models and Other analyses in Attainment Demonstrations for the 8-hour Ozone NAAQS, EPA-454/R-05-002.

Weimer, S., F. Drewnick, O. Hogrefe, J. J. Schwab, K. Rhoads, D. Orsini, M. Canagaratna, D. R. Worsnop, K. L. Demerjian, (2006). Size-Selective Non Refractory Ambient Aerosol Measurements during the PMTACS-NY 2004 Winter Intensive in New York City, J. Geophys. Res., 111, D18205, doi10.1029/2006JD007215.

Figure Captions:

Figure 1. AQFMS model domains and the locations of Pinnacle State Park (PSP) and Queens College (QC).

Figure 2. Time Series and diurnal patterns for relative humidity and temperature from AQFMS predictions and observations at Queens College during July 2001 and January 2004.

Figure 3. Mean Normalized Bias (MNB) for the predictions of daily maximum 8-hr averaged ozone during 3-31 July 2001 (60ppb cutoff value applied to observations).

Figure 4. Hourly time series data for AQFMS predicted and observed O_3, CO, NO_x, SO_2 and NMHC at Queens College during July 2001.

Figure 5. Hourly time series data for AQFMS predicted and observed O_3, CO, NO_x, NO_y, HNO_3 and SO_2 at Pinnacle State Park during July 2001.

Figure 6. Hourly time series data for AQFMS predicted and observed O_3, CO, NO_x and SO_2 at Queens College during January 2004.

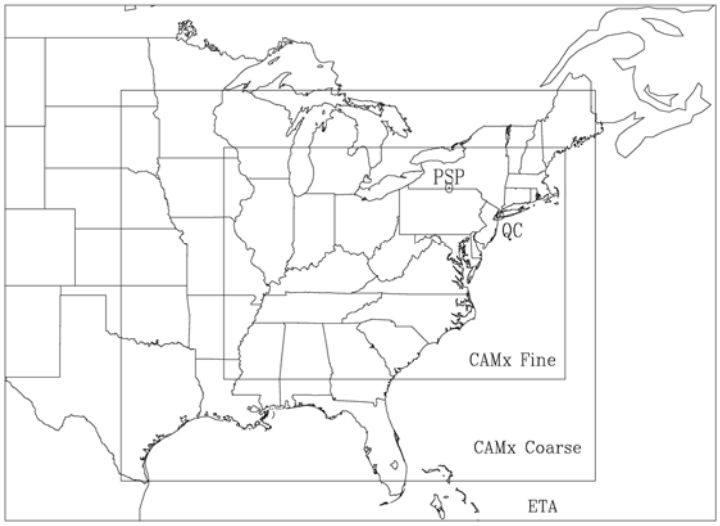
Figure 7. Hourly time series data for AQFMS predicted and observed O_3, CO, NO_x, NO_y HNO_3 and SO_2 at Pinnacle State Park during January 2004.

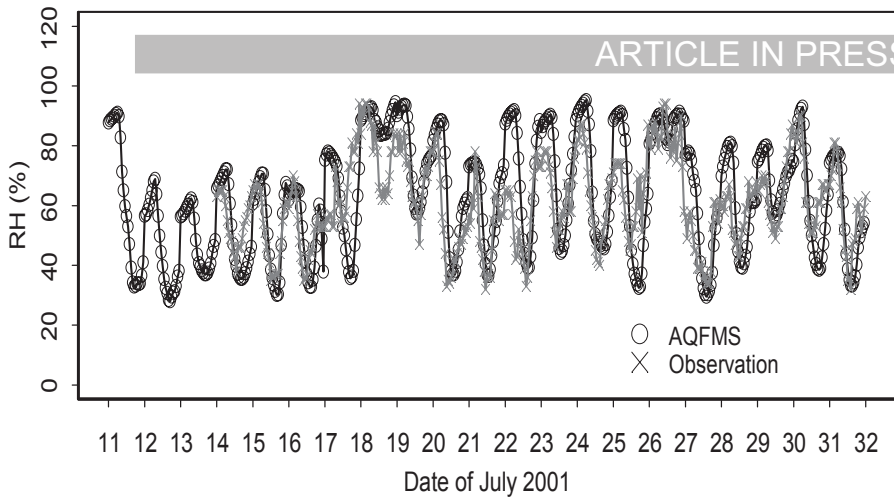
Figure 8. Linear regression for CO vs. NO_x at Queens College, CO vs. NO_y at Pinnacle State Park and O3 vs. NO_z at Pinncle State Park from AQFMS predictions ("A") and observations ("O") during July 2001 (left column) and January 2004 (right column).

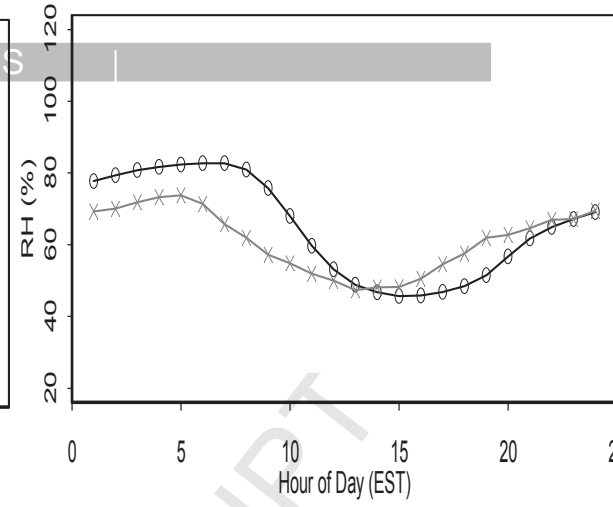
Figure 9. Predicted and observed hourly OH concentrations at Queens College during 14-31 July 2001, top: hourly time series data; bottom: mean diurnal patterns.

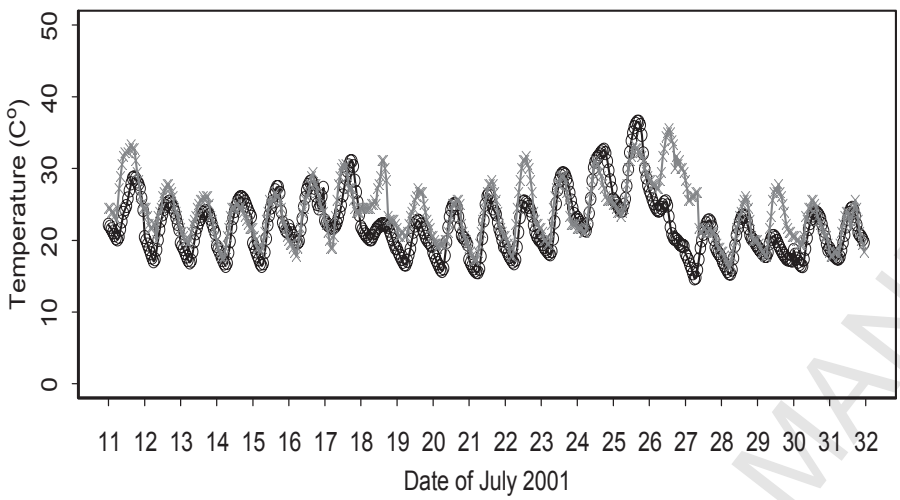
Figure 10. Predicted and observed hourly OH concentrations at Queens College during 14-31 January 2004, top: hourly time series data; bottom: mean diurnal patterns.

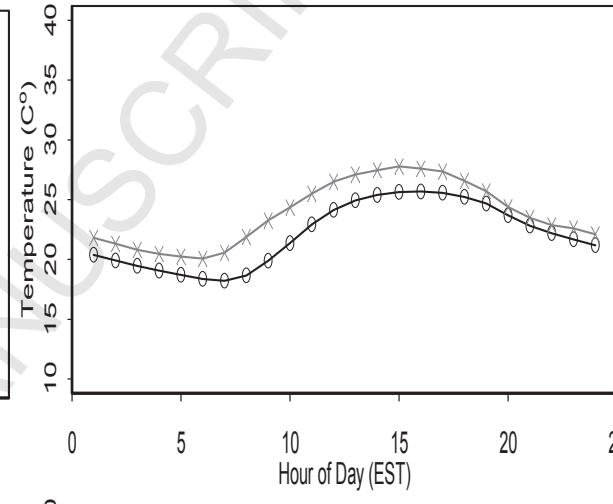
Figure 11. Predicted and observed hourly HONO concentrations at Queens College during 19-31 July 2001 (top) and 17-31 January 2004 (bottom).

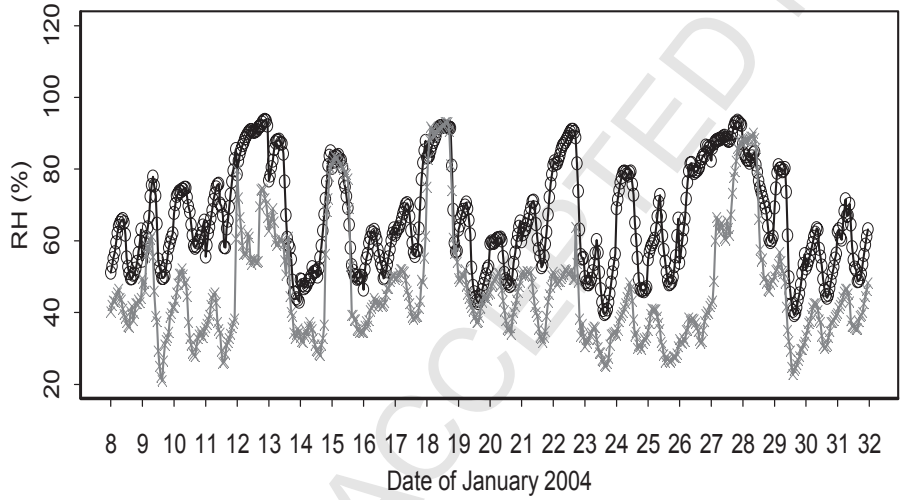


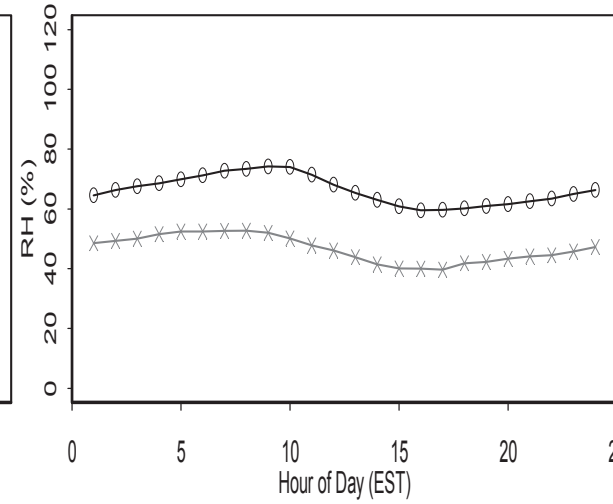


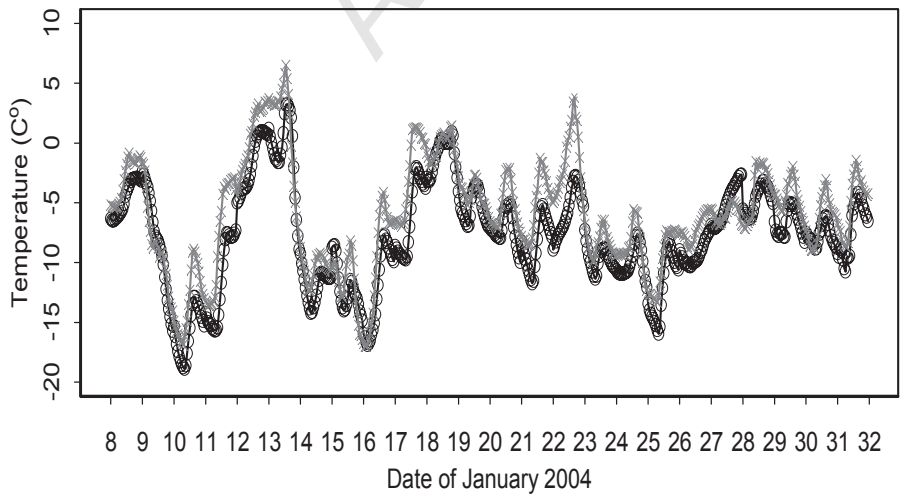


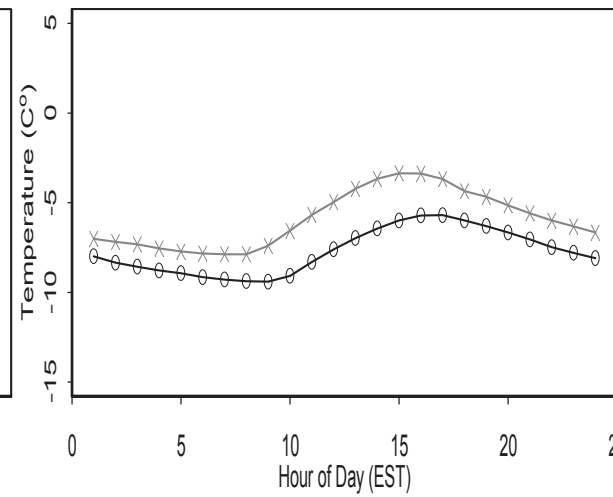












MNB for Maximum 8-hour O3 Predictions (July 2001)