EVALUATION OF AN ANNUAL SIMULATION OF OZONE AND FINE PARTICULATE MATTER OVER THE CONTINENTAL UNITED STATES: WHICH TEMPORAL FEATURES ARE CAPTURED?

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1. INTRODUCTION

Motivated by growing concerns about the detrimental effects of fine particulate matter ($PM_{2.5}$) on human health, the U.S. Environmental Protection Agency (EPA) recently promulgated a National Ambient Air Quality Standard (NAAQS) for $PM_{2.5}$. The $PM_{2.5}$ standard includes a 24-hour limit (65 $\mu g/m^3$ for the 98th percentile) and annual (15 $\mu g/m^3$) limit. Except for a few cases, the annual standard will be the primary concern for attainment issues. Over the next several years, grid-based photochemical models such as the Community Multiscale Air Quality (CMAQ) model (Byun and Ching, 1999) will be used by regulatory agencies to design emission control strategies aimed at meeting and maintaining the NAAQS for O_3 and $PM_{2.5}$. The evaluation of these models for a simulation of current conditions is a necessary prerequisite for using them to simulate future conditions. The evaluation presented in this study focuses on determining the temporal patterns in all components of the modeling system (meteorology, emissions and

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air quality) and comparing them against available observations. Furthermore, we briefly investigated the weekday/weekend differences in the observed and predicted pollutant concentrations and outlined steps for future research. Since anthropogenic emissions are known to have a distinct weekly cycle, such analyses would help us in evaluating the modeling system's ability to accurately reproduce the observed response to emission changes.

2. MODELS AND DATABASE

Meteorological fields for the photochemical simulations were prepared by the MM5 model (Grell et al., 1994) version 3.6.1 over the continental United States at a horizontal resolution of 36 km for the time period from January 1 – December 31, 2001 (McNally, 2003). The MM5 fields were then processed by the Meteorology-Chemistry Interface Program (MCIP) version 2.2. Emissions were processed by the SMOKE processor (Carolina Environmental Programs, 2003) which incorporated the MOBILE6 module (U.S. EPA, 2003) for mobile source emissions and the BEIS3.12 model for biogenic emissions (http://www.epa.gov/asmdnerl/biogen.html). The emission inventory was based on the USEPA National Emissions Inventory for 2001, which relies on state reported values. The seasonality of the ammonia emissions, an important consideration for prediction of $PM_{2.5}$, was estimated based on seasonal information from Gilliland et al. (2003) and Pinder et al. (2004). These meteorological and emission fields were then provided as input to two photochemical models, namely CMAQ (February 2004 version) and REMSAD version 7.061 (ICF Consulting, 2002), both run at a resolution of 36 km over the continental United States. Chemical boundary conditions for both models were prepared from a global simulation with the GEOS-CHEM model (Bey et al., 2001).

This study utilizes a variety of observations from different networks. Observations of surface temperature and wind speed were retrieved from the TDL data set maintained by the Data Support Section at the National Center for Atmospheric Research (NCAR-DSS). Hourly surface ozone observations, hourly $PM_{2.5}$ concentrations measured by tapered element oscillation microbalance (TEOM) monitors (http://www.rpco.com/products/ambprod/amb1400/), and 24-hr average $PM_{2.5}$ concentrations measured at monitors following the Federal Reference Method (FRM) protocol were retrieved from EPA's Air Quality System (AQS) database (http://www.epa.gov/air/data/aqsdb.html). Speciated $PM_{2.5}$ measurements were obtained from the Interagency Monitoring to Protect Visual Environments (IMPROVE) network, the Clean Air Status and Trends Network (CASTNet), and Speciated Trends Network (STN). Because of differences in measurement techniques and instrumentation, sampling frequencies, and site location criteria, model performance was calculated on a species-by-species and network-by-network basis. The analysis presented in this paper focuses on the Eastern United States. Monitoring sites were only included in the analysis if at least 70% of the data were available.

Following the approach outlined in Rao et al. (1997), Hogrefe et al. (2000) and Hogrefe et al. (2001), a spectral decomposition technique was applied to compare temporal variations in observed and predicted time series. To this end, time series of meteorological variables and pollutant concentrations were spectrally decomposed into fluctuations occurring on the intraday (time period less than 12 hours), diurnal (12-48

Table 1a. Correlations between different temporal components embedded in hourly time series of observed and predicted temperature, wind speed, ozone and total $PM_{2.5}$. Median values are shown for each network/variable.

		#Sites	Intra-day		Diurnal		Synoptic		Baseline	
Temperature TDL/MM5		738	0.18		0.90		0.95		0.99	
Wind Speed TDL/MM5		735	0.02		0.60		0.84		0.90	
O_3 AQS/CMAQ		193	0.07		0.70		0.64		0.87	
$PM_{2.5}$ TEOM		67								
CMAQ	REMSAD		0.01	0.03	0.25	0.25	0.70	0.63	0.04	0.10

Table 1b. Correlations between different synoptic and baseline components embedded in time series of observed and predicted $PM_{2.5}$ from different networks. Median values are shown for each network/variable.

	#Sites	Synoptic		Baseline	
		CMAQ	REMSAD	CMAQ	REMSAD
$PM_{2.5}$ FRM (daily)	938	0.68	0.65	0.60	0.51
$PM_{2.5}$ STN (daily)	25	0.60	0.63	0.38	0.35
SO_4 Improve (daily)	44	0.77	0.70	0.89	0.77
SO_4 CASTnet (weekly)	48	0.85	0.72	0.94	0.88
SO_4 STN (daily)	23	0.72	0.70	0.85	0.74
NO_3 Improve (daily)	44	0.46	0.54	0.88	0.78
NO_3 CASTnet (weekly)	48	0.51	0.46	0.89	0.83
NO_3 STN (daily)	23	0.39	0.42	0.83	0.66
NH_4 CASTnet (weekly)	48	0.71	0.72	0.55	0.45
NH_4 STN (daily)	23	0.63	0.66	0.52	0.37
EC STN (daily)	23	0.41	0.39	0.15	0.32
OC STN (daily)	22	0.48	0.55	0.24	0.28
Crustal STN (daily)	23	0.34	0.29	-0.35	-0.39

hours), synoptic (2-21 days) and baseline (greater than 21 days) time scales using the Kolmogorov-Zurbenko (KZ) filter as described in Hogrefe et al. (2000). Note that the intraday and diurnal components could only be estimated for variables measured hourly, while the synoptic and baseline components could be estimated for variables measured hourly, daily or weekly. All analyses presented in this paper were performed over the entire annual cycle from January 1 – December 31, 2001, with the exception of the ozone weekday/weekend analysis which was performed for June 1 – August 31, 2001.

3. RESULTS AND DISCUSSION

3.1. Correlations on different time scales

Correlations between different temporal components embedded in time series of the observed and predicted variables were computed for temperature, wind speed and ozone as well as total and speciated $PM_{2.5}$ from the different measurement networks (Tables 1a-b). The correlations were computed at each site for a given variable/network/model combination, and Tables 1a-b list the median value of the correlation across all sites for a given variable/network/model combination. For the meteorological variables (temperature and wind speed), correlations increase with increasing time scale, i.e.

correlations are lowest for the intra-day component ($r < 0.2$) and highest for the baseline component ($r > 0.9$).

While correlations are relatively high for the diurnal component ($r > 0.6$), part of this correlation is due to the inherent cyclical nature of this component, and correlations are lower when the time series of the diurnal amplitudes are considered (not shown). It is not surprising that the correlation is highest on the synoptic and baseline time scale since MM5 model predictions were nudged towards analysis fields using 4-Dimensional Data Assimilation techniques. For ozone, correlations follow a similar pattern as temperature and wind speed, with correlations on the intraday time scale being less than 0.1 and correlations on the baseline time scale being 0.87. The results presented here are consistent with those presented in Hogrefe et al. (2001) who analyzed ozone from a three-months summertime simulation over the Eastern United States.

Except for hourly measurements of total $PM_{2.5}$ by TEOM instruments retrieved from EPA's AQS, all $PM_{2.5}$ measurements analyzed in this study are based on filter samples of either 24-hr average or 7-day average concentrations. Consequently, the intra-day and diurnal components could only be estimated for the comparison of CMAQ and REMSAD model predictions with total $PM_{2.5}$ measurements by TEOM instruments. It is striking that the correlations between TEOM observations and model predictions are poor on the diurnal and baseline components for both CMAQ and REMSAD. Figures 1 a and b show the average observed and predicted diurnal cycles and the time series of the observed and predicted baseline components averaged over all TEOM monitors and corresponding model grid cells. Although the time of occurrence of maxima are simulated well, there is a large difference in the amplitude of the diurnal forcing; both models overestimate observations during nighttime and severely underestimate observations during daytime hours. Plausible reasons for this discrepancy are misrepresentations of the strength of vertical mixing in the model or the magnitude of primary $PM_{2.5}$ emissions from area and mobile sources. Figure 1b illustrates that the low correlations on the baseline time scale stem from the higher $PM_{2.5}$ predictions by both models during wintertime while TEOM measurements show a decrease. Part of this decrease in TEOM measurements during wintertime is likely caused by the high operating temperatures of most of the currently-deployed TEOM instruments (30ºC and 50ºC). Volatilization losses can occur when the sample is heated from ambient temperature to the operating temperature, and such losses tend to be higher during colder ambient temperatures (Allen et al., 1997). On the other hand, CMAQ and REMSAD utilize MM5-simulated temperatures to calculate the partitioning between gas and particle phase. In other words, there is an inherent difference between measurement technique and modeling approach, and this difference exhibits seasonality, thereby affecting the baseline comparisons. Support for this explanation comes from the higher baseline correlations when CMAQ and REMSAD are compared against $PM_{2.5}$ filter observations from FRM monitors and the STN network. This highlights the importance of conducting $PM_{2.5}$ model evaluation on a network-by-network basis. In other words, data from different air monitoring networks should not be combined into a single dataset for the purpose of model evaluation.

Correlations between the synoptic and baseline components of sulfate measured by the IMPROVE, CASTNet, and STN networks, and predicted by CMAQ and REMSAD are consistently greater than 0.7, with baseline correlations exceeding 0.85 for CMAQ and 0.74 for REMSAD. It is noteworthy that there is relatively little difference in model

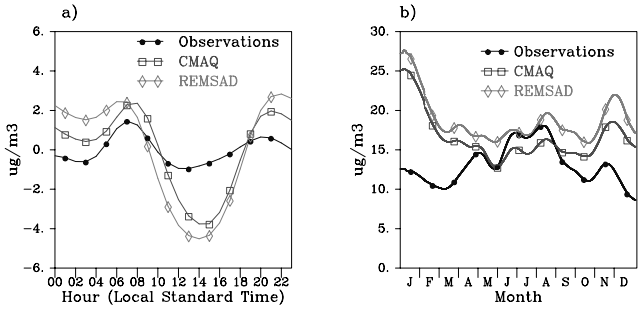

Figure 1: a) Average observed and predicted diurnal cycles and b) time series of the observed and predicted baseline components averaged over all TEOM monitors and corresponding model grid cells for $PM_{2.5}$.

performance across the different networks, a finding that is consistent with the regional-scale nature of sulfate concentrations in the eastern United States that has also been discussed by Gego et al. (2004). Furthermore, correlations for REMSAD are consistently lower than those for CMAQ for this pollutant across all networks. For nitrate, correlations on the baseline time scale are similar to those for sulfate, but correlations on the synoptic time scale are lower. For the baseline, CMAQ correlations are consistently higher than those for REMSAD.

In contrast to baseline correlations for sulfate and nitrate, correlations are relatively low for ammonium. A likely contributor to these lower correlations is the seasonal characterization of NH_3 emissions. The seasonality for NH_3 emissions is a well-known uncertainty that is currently being investigated from both bottom-up inventory development and from top-down estimation methods (Gilliland et al., 2003). An inverse modeling study is underway using this 2001 annual simulation to consider how the current seasonality estimates for NH_3 emissions should be modified to improve model predictions of ammonium aerosols and wet deposition.

Model predicted concentrations of elemental carbon (EC), organic carbon (OC), and crustal material are strongly influenced by emissions of primary PM since there is no secondary formation mechanism for EC and crustal material in CMAQ and REMSAD. Consequently, the relatively weak correlations between the observed and predicted

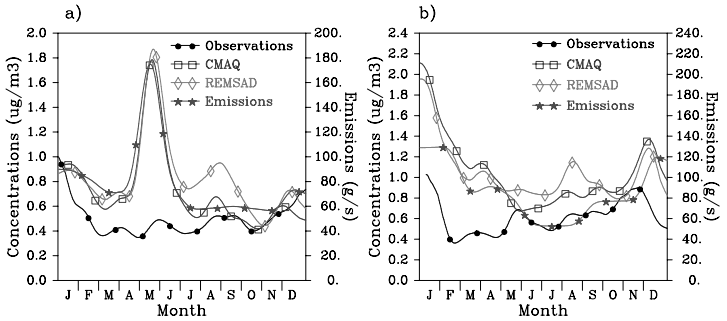

Figure 2: Baseline of EC observations, CMAQ and REMSAD predictions, and $PM_{2.5}$ emissions a) Decatur, Georgia b) Bronx, New York

baseline components for these species point to potential problems in the temporal allocation of PM emissions during emission processing. To investigate this issue, we constructed the baseline component of EC observations, CMAQ and REMSAD predictions, and total $PM_{2.5}$ emissions at several STN monitoring locations. Examples of this analysis are shown in Figures 2a and b. The strong correlation between $PM_{2.5}$ emissions and model-predicted EC concentrations is clearly visible at the Decatur, GA monitor and, to a slightly lesser extent, at the Bronx, NY monitor. In both cases, the relatively poor correlation between observations and model predictions seems to be largely driven by temporal signature of the $PM_{2.5}$ emissions. Therefore, in order to improve model performance on longer time scales for primary species such as EC and crustal material, it is necessary to improve the temporal characterization of primary $PM_{2.5}$ emissions.

In summary, the results presented in Tables 1a-b illustrate that the models exhibit greatest skills at capturing longer-term (seasonal) fluctuations for temperature, wind speed, ozone, sulfate and nitrate. For total $PM_{2.5}$, ammonium, EC, OC and crustal $PM_{2.5}$, correlations are highest for the synoptic time scale, implying problems with factors other than meteorology in capturing the baseline fluctuations. For the variables for which hourly measurements were available, correlations were insignificant on the intraday time scale, suggesting that these models are not skillful in simulating the shorter-term variations in pollutant levels.

3.2. Analysis of the weekday/weekend effect

Anthropogenic emissions of NO_x and VOC are reduced on weekends due to reduced traffic as well as industrial and commercial activities. The impact of these cyclical reductions of precursors on ozone has been the subject of numerous studies (e.g. Cleveland et al., 1974; Croes et al., 2003). Many studies found ozone increases on weekends in urban core areas and laid out several hypotheses explaining this behavior, including reduced O_3 titration by NO and more efficient ozone production on weekends. One of the main motivations for such studies is to infer the likely response of ozone concentrations to emission control policies from these cyclical real-world emission reductions. While there is no direct way to evaluate photochemical model responses to hypothetical emission control scenarios, analysis of the weekday/weekend effect could provide a tool to evaluate the modeling system's ability to accurately reproduce the observed response to emission changes. While performing such analysis in sufficient detail is beyond the scope of this paper and will be presented in future work, we briefly outline some of the necessary steps in performing this analysis.

As a first step, it is necessary to establish that the weekday/weekend effect indeed exists during the period of analysis in both observations and model predictions. To this end, average weekly cycles need to be computed for each station, and the difference between average weekday (Monday-Friday) and weekend (Saturday-Sunday) concentrations needs to be determined. As an example, Figure 3 presents a scatter plot of the average CMAQ predicted difference between weekend daily maximum 1-hr ozone concentrations and weekday daily maximum 1-hr ozone concentrations versus the corresponding difference computed from observations at the same location. This figure illustrates that a weekday/weekend cycle of comparable magnitude is indeed present in observed and CMAQ-predicted ozone concentrations during the summer of 2001.

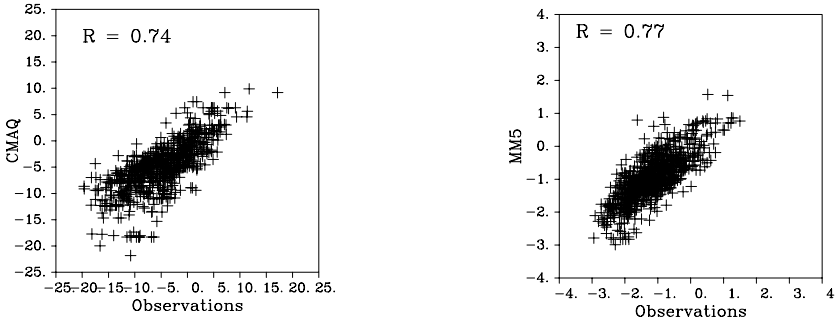

Figure 3: a) Scatter plot of the average CMAQ predicted difference between weekend daily maximum 1-hr ozone concentrations and weekday daily maximum 1-hr ozone concentrations versus the corresponding difference computed from observations at the same location. b) As in a), but for daily maximum temperature.

Additional analyses are needed to determine the location of stations that show opposite magnitudes of the weekday/weekend differences, to perform analysis on early morning concentrations (when the difference in motor vehicle emissions between weekdays and weekends is most pronounced), to restrict analysis to high ozone days only, and to include analysis of ozone precursors as well. Furthermore, it is important to ascertain whether the weekday versus weekend differences in ozone concentrations are caused by emission fluctuations or might be largely explained by meteorological effects when analysis is restricted to a single summer season only. Indeed, Figure 3b shows that for the summer of 2001 there was a distinct weekday/weekend fluctuation in temperature at most monitors in the eastern U.S. Most monitors show lower daily maximum temperatures on weekends than on weekdays, and MM5 captures this behavior. Because temperature both directly influences the rate of ozone formation and serves as a proxy for other meteorological parameters conducive to ozone formation, this figure illustrates that the existence of a weekday/weekend cycle in ozone concentrations for the summer of 2001 (Figure 3a) can not unequivocally be attributed to cyclical changes in precursor emissions. In the absence of longer time records of observed and predicted ozone concentrations, one might be able to apply statistical techniques to adjust observed and predicted ozone concentrations for meteorological variability to isolate the effect of emission reductions. Also, it is important to include an analysis of weekday/weekend differences in the processed emission files in the overall evaluation of the modeling system's ability to simulate this phenomenon.

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5. DISCLAIMER

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