



Evaluating the performance of regional-scale photochemical modeling systems. Part III—Precursor predictions

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Abstract

Two regional-scale photochemical modeling systems, RAMS/UAM-V and MM5/MAQSIP, are used to simulate precursor concentrations for 4 June–31 August 1995 period. The time series of simulated and observed precursor concentrations are spectrally decomposed into intra-day, diurnal, synoptic, and longer-term (baseline) forcings and compared on each time scale. The results reveal that the observed and modeled precursor concentrations are uncorrelated on the intra-day time scale for both modeling systems while correlations are higher on longer time scales. In observations, the variability in NO_x concentrations is dominated by the diurnal and synoptic-scale processes, while NO_y is found to vary most on the synoptic time scale. In observations of volatile organic compounds (VOCs), the variability is dominated by the diurnal and synoptic processes for both biogenic and anthropogenic hydrocarbons. The pattern seen in the observations, in terms of the relative contribution of different temporal components to the total variance, is better captured by the two modeling systems for NO_y than for NO_x and VOCs. There are differences between model predictions and observations in terms of the actual magnitudes of variances of each temporal component. These results suggest the need to cover longer time periods in modeling simulations to resolve longer-term processes, because they seem to play a dominant role in dictating the precursor variability. © 2001 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Ground-level concentrations of ozone exceeding the air quality standards set forth by the US Environmental Protection Agency (US EPA) are a cause for concern

because of their adverse effects on human health and vegetation. Ozone within the troposphere is produced through the photochemical oxidation of nitrogen oxides (NO_x) and volatile organic compounds (VOCs). The chemical processes of ozone formation have been well documented (e.g. Seinfeld, 1986; Finlayson-Pitts and Pitts, 1986; NRC, 1991). Polluted urban environments have abundantly available NO_x and VOC concentrations to sustain ozone production. In rural areas, elevated levels of ozone may be a result of transport of ozone from polluted environments, and in situ production through reactions involving transported NO_x and locally emitted natural VOCs (McKeen et al., 1991). Thus, the variability in ozone and precursor concentrations is dictated not only by the short-term processes

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such as fluctuations in fresh emissions and local meteorological conditions, but also by atmospheric transport processes that occur on longer time scales. An examination of the variability in the precursor concentrations and time scales that contribute to this variability would help us in improving our understanding of the ozone process.

In the United States, the non-attainment of ozone standards is not restricted to urban centers and often occurs on a regional scale (Chameides et al., 1997). Emission control strategies are being designed to bring air quality into compliance with the ozone standards using photochemical model simulations of historical episodic events (Tesche et al., 1996). The performance of these models is usually evaluated by comparing the observed and simulated concentrations of ozone only. However, it is possible for the model to predict reasonable ozone values, but there may still be considerable uncertainty in the prediction of the sensitivity of ozone reductions to reductions in NO_x and VOC (Sillman, 1995). Accurate predictions of ozone and the NO_x -VOC sensitive regimes depend on the success of the photochemical model in reproducing the observed spatio-temporal behavior of precursor concentrations. Therefore, we examine the spatial and temporal characteristics of the modeled and observed precursor concentrations.

Rao et al. (1997) and Porter et al. (2001) showed that the information contained in the time series of daily maxima of 1-h ozone can be physically interpreted by separating the scales of motion embedded in the data, namely, short-term (weather-related) fluctuations, seasonal (solar-induced) variations, and long-term (climate-policy related) changes. In this study, we examine the hourly concentrations of simulated and observed precursor concentrations over a period of three months on the following time scales of interest; intra-day (periods < 12 h), diurnal (period of 24 h), synoptic (period of 2–21 days), and longer-term (periods longer than 21 days) time scales as in Hogrefe et al. (2000). These time scales are related to dominant dynamical processes that contribute to the variability in the precursor concentrations over a 3-month time period. Injection of fresh emissions and local transport occur on the intra-day scale. Variations on the diurnal scale occur due to the influence of solar insolation on photochemical reaction rates while synoptic-scale fluctuations are attributable to meteorological processes such as the passage of mid-latitude cyclones and fronts. The longer-term variations can be related to the varying efficiency of wet and dry deposition rates due to seasonal changes in precipitation amounts and vegetation cover and the seasonal cycle of solar insolation intensity leading to variations in biogenic emissions.

While grid-based photochemical models represent a significant improvement over the earlier one-dimen-

sional Lagrangian models, they have several limitations which affect the proper representation of precursors, and consequently, ozone predictions. The lack of sufficient vertical and horizontal resolution, uncertainties in the boundary layer parameterization, representation of clouds, biogenic emission rates, etc. are some of the limitations in the current models (McKeen et al., 1991). Since the evolution of precursors in the models is governed by the prescribed emission rates as well as the chemical and physical processes considered in the model, it is important to assess model performance using precursors in addition to ozone in order to better understand the ozone process. Several studies have investigated the relationship between ozone and its precursors in urban and rural environments (e.g. Chameides et al., 1988, 1992; Liu et al., 1987). While comparisons of modeled and observed ozone and precursors have been performed in the past, they have been restricted to individual episodes lasting 2–5 days and aimed mainly at evaluating the accuracy of ozone predictions (e.g. Tesche et al. 1996; Roselle and Schere, 1995). In this paper, we analyze precursor concentrations on multiple temporal scales during an entire summer season and examine the ability of the photochemical model to reproduce the observed variability in the precursors. The period of interest for this study is the summer of 1995 which included three major episodes with elevated ozone levels over large portions of the eastern United States.

2. Databases and model descriptions

2.1. Databases

Measured hourly concentrations of NO_x ($\text{NO} + \text{NO}_2$), VOC, and NO_y (total reactive nitrogen oxides) are extracted from EPA's Aerometric Information Retrieval System (AIRS) database. Additional data sets are obtained from the 1995 NARSTO-NE database archived at the NASA Langley Research Center's EOSDIS Distributed Active Archive Center, and the Harvard Forest site in Central Massachusetts. The location of the sites with measurements of NO_x and NO_y are shown in Fig. 1a and the location of the sites with measurements of isoprene, toluene, ethene and xylene are shown in Fig. 1b. These monitoring sites have been selected because of the availability of continuous precursor concentration data for the summer of 1995. The number of sites according to the availability of species data is as follows: 63 sites for NO_x , 4 sites for NO_y , 8 sites for isoprene, 7 sites for ethene, 3 sites for xylene, and 3 sites for toluene.

Modeled precursor concentrations were obtained from two seasonal simulation with the RAMS/UAM-V and MM5/MAQSIP modeling systems.

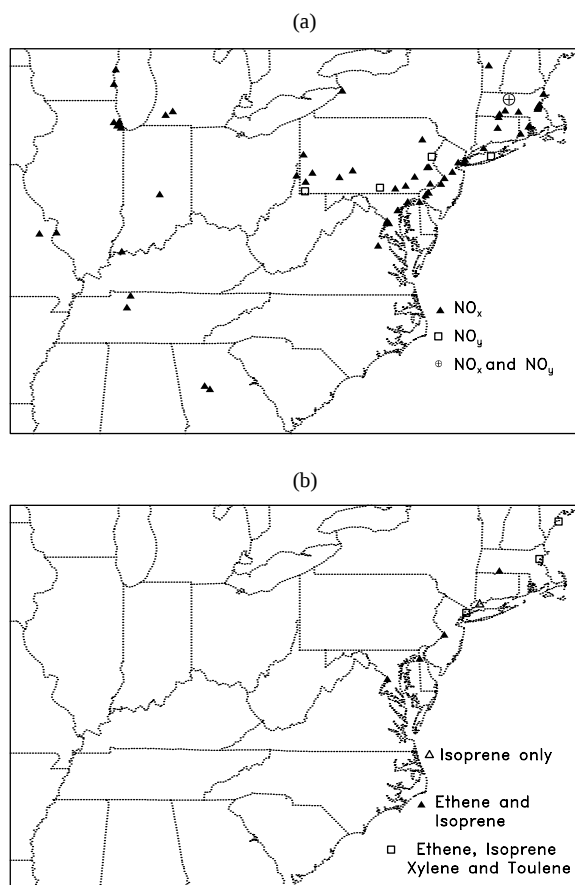


Fig. 1. Observational sites considered in the study.

The Urban Airshed Model—Variable Grid Version (UAM-V) (SAI, 1995) is a three-dimensional grid-based, photochemical model; in the simulation analyzed here, UAM-V version 1.24 including the fast chemistry solver and updated isoprene chemistry (SAI, 1995) was used. The UAM-V has been extensively used in the past for regulatory purposes (OTAG, 1997). The model simulations were performed from 1 June to 31 August 1995 in a non-nested mode with a horizontal gridcell dimension of 36 km in a domain extending from 99°W to 67°W and from 26°N to 47°N. The vertical structure in the model consisted of 14 vertical layers extending from the surface up to 4 km. The meteorological input for the UAM-V was obtained from simulations using the Regional Atmospheric Modeling System (RAMS) Version 3b. Details relating to meteorological modeling with RAMS3b can be found in Lagouvardos et al. (1997). Details regarding the set up of the model can be found in Hogrefe et al. (2001a). Pielke and Uliasz (1998) discussed the issues relating to the application of RAMS3b to regional air quality simulations.

The second modeling system considered in this study is the Seasonal Model for Regional Air Quality

(SMRAQ) (SMRAQ, 1997; Kasibhatla and Chameides, 2000). The photochemical modeling system used in this case is the Multiscale Air Quality Simulation Platform (MAQSIP) (Odman and Ingram, 1996) which is a generalized coordinate, multiscale air quality modeling system. It is built as a prototype for EPA's Models-3 system which adopted some features from the SARMAP Air Quality Model (SAQM) (Chang et al., 1997). The modeling simulations were carried out for the period 15 May–13 September 1995 which also covered the time period of the RAMS3b/UAM-V simulations. The model was run in a non-nested mode with horizontal grid dimensions of 36 km. There are 22 sigma levels extending up to 100 mb in the vertical direction with 11 layers below 1500 m. In the horizontal, the grid projection is Lambert Conformal; the modeling domain covers most of the eastern United States (Kasibhatla and Chameides, 2000). Further details on the MAQSIP modeling system can be found in Wheeler et al. (1998) and Kasibhatla and Chameides (2000). The meteorological input data for MAQSIP was derived from the NCAR/Penn State Fifth Generation Mesoscale Meteorological Model (MM5)—version 1 (Grell et al., 1994). Additional details on the setup of MM5 for the simulation analyzed here can be found in Hogrefe et al. (2001a).

Both modeling systems used the Carbon Bond Mechanism (Gery et al., 1989), version 4.2 which incorporates three additional radical terminal reactions for XO₂N chemical mechanisms for low NO_x conditions and has a rate coefficient for the XO₂N + NO reaction that was increased by a factor of 12. Further details on this modification can be found in Kasibhatla et al. (1997). The boundary conditions were treated differently in the two modeling systems in the case of ozone. For the UAM-V, time-varying boundary conditions were used based on surface observations and available ozonesonde data. For chemical species other than ozone, time-invariant background concentrations were used. In the case of MAQSIP, time-invariant boundary conditions were used for ozone as well as other species. Since the temperatures and solar insolation derived from the two meteorological models are different, the modeled biogenic and mobile source emissions input to the two air quality models also differed somewhat. The preparation of the emission inventory for the UAM-V photochemical modeling simulation has been described in Sistla et al. (2001). The emissions inventory for MAQSIP was based on the Sparse Matrix Operator Kernel Emissions (SMOKE) (Houyoux et al., 1996) and is described in Houyoux et al. (2000).

The modeling simulations analyzed in this study have been performed as part of separate studies by different groups (Sistla et al., 2001; Kasibhatla and Chameides, 2000) with no accord on the modeling options. For example, to study the impact of chemistry on the precursor predictions, it would be useful to perform

additional seasonal simulations using either RAMS or MM5 to drive both photochemical models. Similarly, to study the effect of meteorology on precursor predictions, it would be useful to carry out model simulations using both the meteorological models to drive one photochemical model (either MAQSIP or UAM-V). Since such simulations have not been performed, detailed analyses of the impact of individual processes such as emissions, meteorology and chemistry on precursor predictions on different time scales is beyond the scope of this paper.

2.2. Methods of analysis

Analyses presented in this study are based on hourly data from observational sites and model grid points within the domain of interest. Modeled concentrations are obtained at the corresponding grid cells containing the observational sites in both modeling systems. Correlations among the variables are computed in the form of standardized regression coefficients, which allows us to compare the relative magnitudes of the correlations between variables that might have different variances. The regression coefficient can then be interpreted as the covariance between the two standardized variables under consideration. The spatial correlation structure associated with each temporal component is determined by computing the correlation coefficient for all pairs of sites as in Hogrefe et al. (2001a, b).

2.3. Traditional statistical methods

Although there are no guidelines set by EPA to evaluate model performance in simulating the precursor concentrations, traditional statistical measures recommended for urban-scale ozone models (US EPA, 1991) have been applied in this study to evaluate the predictions of precursor (NO_x) concentrations from both modeling systems. The statistical measures considered here are the mean normalized bias error (MNBE), mean normalized gross error (MNGE), and unpaired peak accuracy (UPA). While MNBE and MNGE indicate the overall performance of the models, UPA represents the model's ability to simulate the peak

precursor concentrations. In this case, the statistical sampling was done for the entire summer season over all observational sites (i.e. sampling through space and time). Since MNBE and MNGE are normalized with respect to the observed precursor concentration at each hour, cutoff levels in the observations have been used to avoid contamination of statistics (Russell and Dennis, 2000). For a satisfactory model performance, EPA recommended values of 5–15% for MNBE, 30–35% for MNGE and 15–20% for UPA for ozone predictions. The results in Table 1 reveal that the error values for precursor concentrations from both modeling systems are much higher than those for ozone predictions presented in Hogrefe et al. (2001a). The RAMS/UAM-V modeling system appears to perform better than MM5/MAQSIP if we consider MNBE, but the performance of both modeling systems is comparable if MNGE is considered. In the past, these statistics were used for model evaluation for episodic days only (Russell and Dennis, 2000). The statistical metrics for the seasonal evaluation of model behavior seem to provide little insight into the model's ability to capture the spatial and temporal variability embedded in the observations on different time scales. Therefore, as in Hogrefe et al. (2001a), we perform time series analysis in an effort to evaluate behavior of precursor concentrations as indicated below.

2.4. Spectral decomposition of precursor concentrations

Following Hogrefe et al. (2000), time series of hourly precursor concentrations are spectrally decomposed using the Kolmogorov–Zurbenko (KZ) filter, which is a high resolution filter that can preserve information in the presence of unevenly distributed and missing data (Zurbenko 1986, 1991). The KZ filter is an iterated moving average low pass filter (Rao and Zurbenko, 1994). The transfer function of this filter is determined by two parameters; the number of iterations, k and the averaging window length, m (Eskridge et al., 1997). Thus, the KZ_{mk} filter is defined as k iterations of a centered moving average of m points. Rao et al. (1997) discussed the characteristics of the KZ filter and described the procedure to estimate the filter parameters

Table 1
EPA-recommended statistical measures for NO_x predictions

	Cutoff 60 ppb		Cutoff 40 ppb		Cutoff 20 ppb	
	UAM-V vs. obs	MAQSIP vs. obs	UAM-V vs. obs	MAQSIP vs. obs	UAM-V vs. obs	MAQSIP vs. obs
MNBE	−18	−71	−5	−65	17	−57
MNGE	63	72	69	68	82	63
UPA	71	−67	71	−67	71	−67

for any given time scale. The number of iterations (k) and the window lengths (m) used in the spectral decomposition of precursors were based on the cut off frequencies used in the case of ozone (see Hogrefe et al., 2000a). They also represent the frequencies separating the physical scales of the observed hourly precursor data as shown in the next section from the power spectrum of hourly precursor data. The spectral decomposition of precursors is accomplished as follows:

$$\begin{aligned} ID(t) &= P_L(t) - KZ_{3,3} [P_L(t)], \\ DI(t) &= KZ_{3,3} [P_L(t)] - KZ_{13,5} [P_L(t)], \\ SY(t) &= KZ_{13,5} [P_L(t)] - KZ_{103,5} [P_L(t)], \\ BL(t) &= KZ_{103,5} [P_L(t)], \end{aligned} \quad (1)$$

where $P_L(t)$ is the natural logarithm of precursor concentrations, $ID(t)$ is the intra-day component, $DI(t)$ is the diurnal component, $SY(t)$ is the synoptic

component, and $BL(t)$ is the longer-term (baseline) component. The log-transformation of the original time series, prior to the application of the KZ filter, helps to stabilize the variance and reduce non-linear effects (Rao et al. 1997; Hogrefe et al. 2000). The original, unfiltered precursor concentration, $P(t)$, is related to the spectral components as follows:

$$P(t) = e^{ID(t)} \times e^{DI(t)} \times e^{SY(t)} \times e^{BL(t)}. \quad (2)$$

2.5. Filter cut-off frequencies

The power spectra of hourly NO_x and NO_y concentrations observed over the 1991–1996 period, and hourly isoprene and ethene for the 1992–1995 period at the Harvard Forest site in Central Massachusetts were constructed, and the periodograms were smoothed with the algorithm developed by DiRienzo and Zurbenko (1999) (see Fig. 2). Any information at a particular frequency, ω , is reflected by a sharp change in the

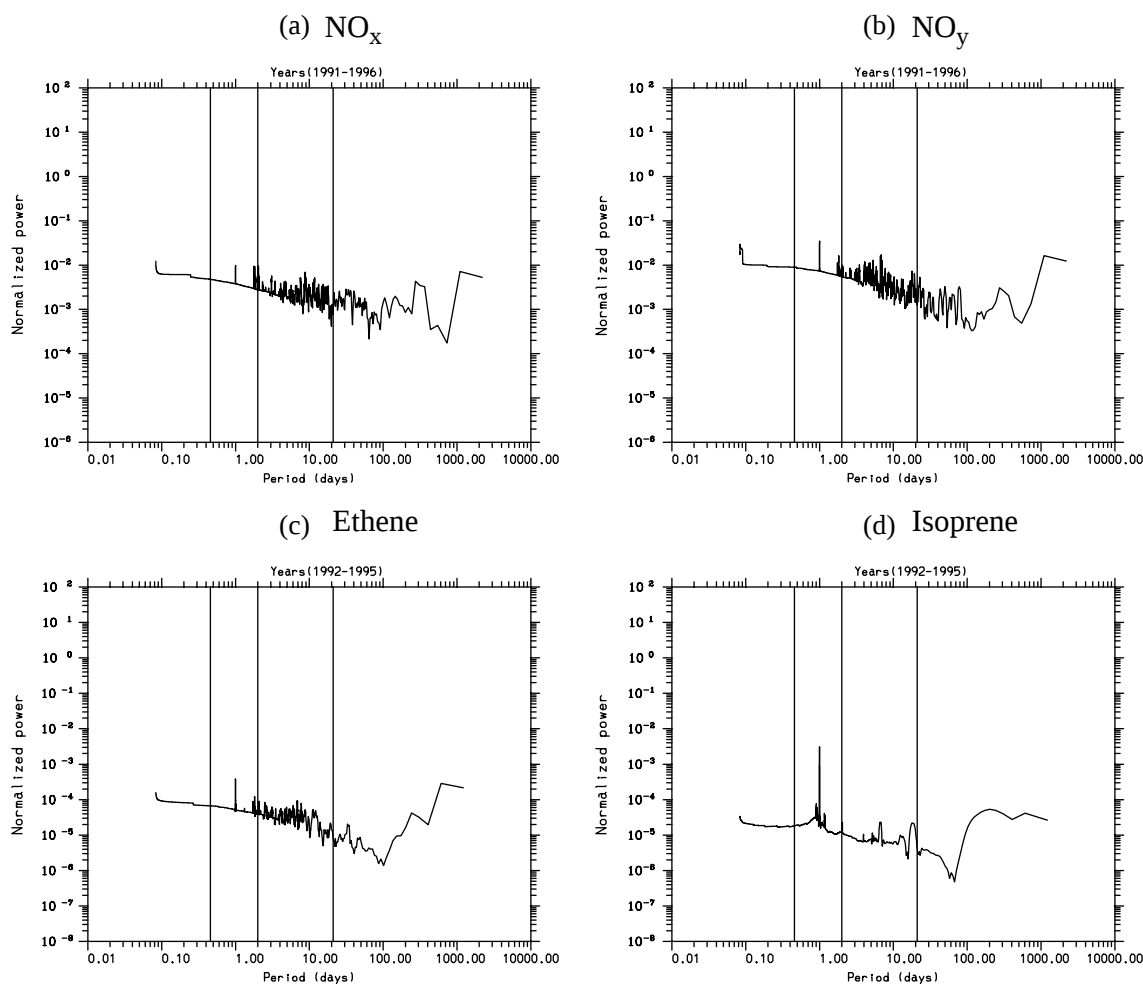


Fig. 2. Power spectrum of NO_x , NO_y , ethene and isoprene at the Harvard Forest site in Central Massachusetts.

spectra, resulting in the construction of a spectral estimate with variable window width. Details regarding the selection of the filter's window width were discussed by Rao et al. (1997).

Figs. 2a and b depict the smoothed periodograms of NO_x and NO_y , respectively, while Figs. 2c and d depict the smoothed periodograms of ethene and isoprene, respectively. The vertical lines in Fig. 2 represent the cutoff (separation point) between the high-frequency and low-frequency components (see Hogrefe et al., 2000). From Figs. 2a and b, it is evident that there is prominent energy in the power spectrum on the diurnal scale within the cutoff periods (11 h–2 days) and notable energy on the synoptic-scale within the cutoff period (2–21 days). The power spectra reveal the presence of significant energy in time scales > 21 days in both NO_x and NO_y (Figs. 2a and b, respectively). In the period-

ograms of ethene and isoprene (Figs. 2c and d), prominent peaks are seen on the diurnal scale. The results also reveal the presence of energy on the longer time scales in both VOC species.

3. Results and discussion

3.1. Observed and modeled NO_x

To evaluate model performance, the square of the coefficient of correlation (RSQ) between the observed and modeled NO_x was computed for each site, and the results are presented in Figs. 3 and 4 for RAMS/UAM-V and MM5/MAQSIP, respectively. In the panel for the raw (i.e. unfiltered) data, it can be seen that the sites along the urban corridor in the northeast have a slightly

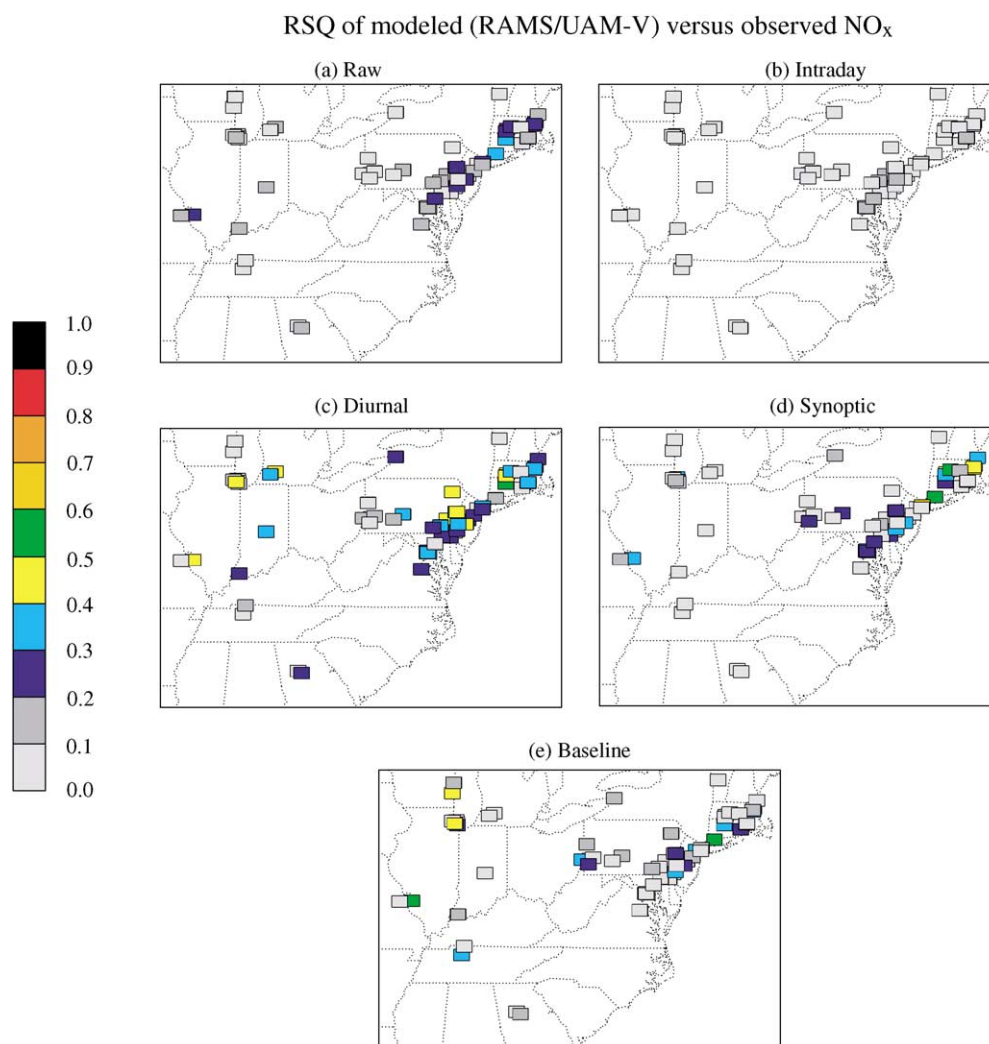


Fig. 3. Square of the correlation coefficient between observed and modeled NO_x in RAMS/UAM-V for different time scales.

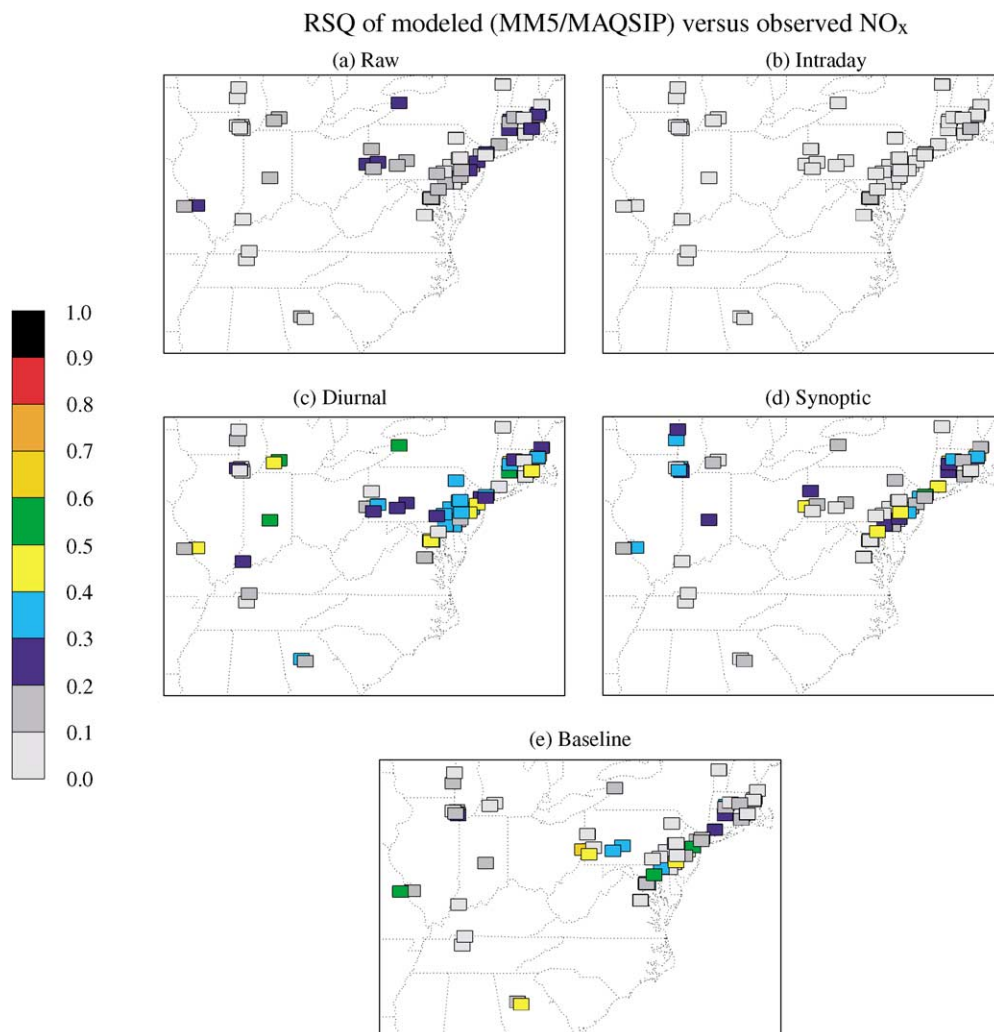


Fig. 4. Square of the correlation coefficient of between observed and modeled NO_x in MM5/MAQSIP for different time scales.

higher correlation than in the Midwest and Southeast for both modeling systems. On the intra-day time scale, the observations and model predictions are poorly correlated with RSQ values lower than 0.1 at all the sites for both models. Correlations improved for the diurnal component; a relatively higher percentage of sites are associated with RSQ values in the range 0.4–0.6 on this time scale. Most of the sites with higher correlations are along the northeastern urban corridor. The results reveal that the observed and modeled NO_x concentrations are better correlated on the diurnal, synoptic and baseline time scales than on the intra-day time scale. The region-to-region differences in correlations between the two modeling systems are evident for the diurnal, synoptic and baseline components (Figs. 3 and 4).

The differences in the energy in the observed and modeled NO_x for each temporal component are

examined by computing the ratio of the modeled and observed variance as presented in Figs. 5 and 6. For the unfiltered data, the MM5/MAQSIP system (Fig. 6a) predicted higher ratios of variance with respect to the observations, with a significant number of sites showing higher ratios compared to the RAMS/UAMV system (Fig. 5a). The variances on the intra-day, diurnal and synoptic components are overestimated in the MM5/MAQSIP system for a number of sites (Figs. 6b–d). The ratios are highest on the diurnal scale at about 90% of the sites, indicating that the diurnal forcing in the model is significantly overestimated (Fig. 6c). On the other hand, the model-predicted diurnal variance is higher at about 70% of the sites in the case of RAMS/UAM-V (Fig. 5c), indicating that the modeling system overestimated the diurnal forcing, though not as much as MM5/MAQSIP (Fig. 6c).

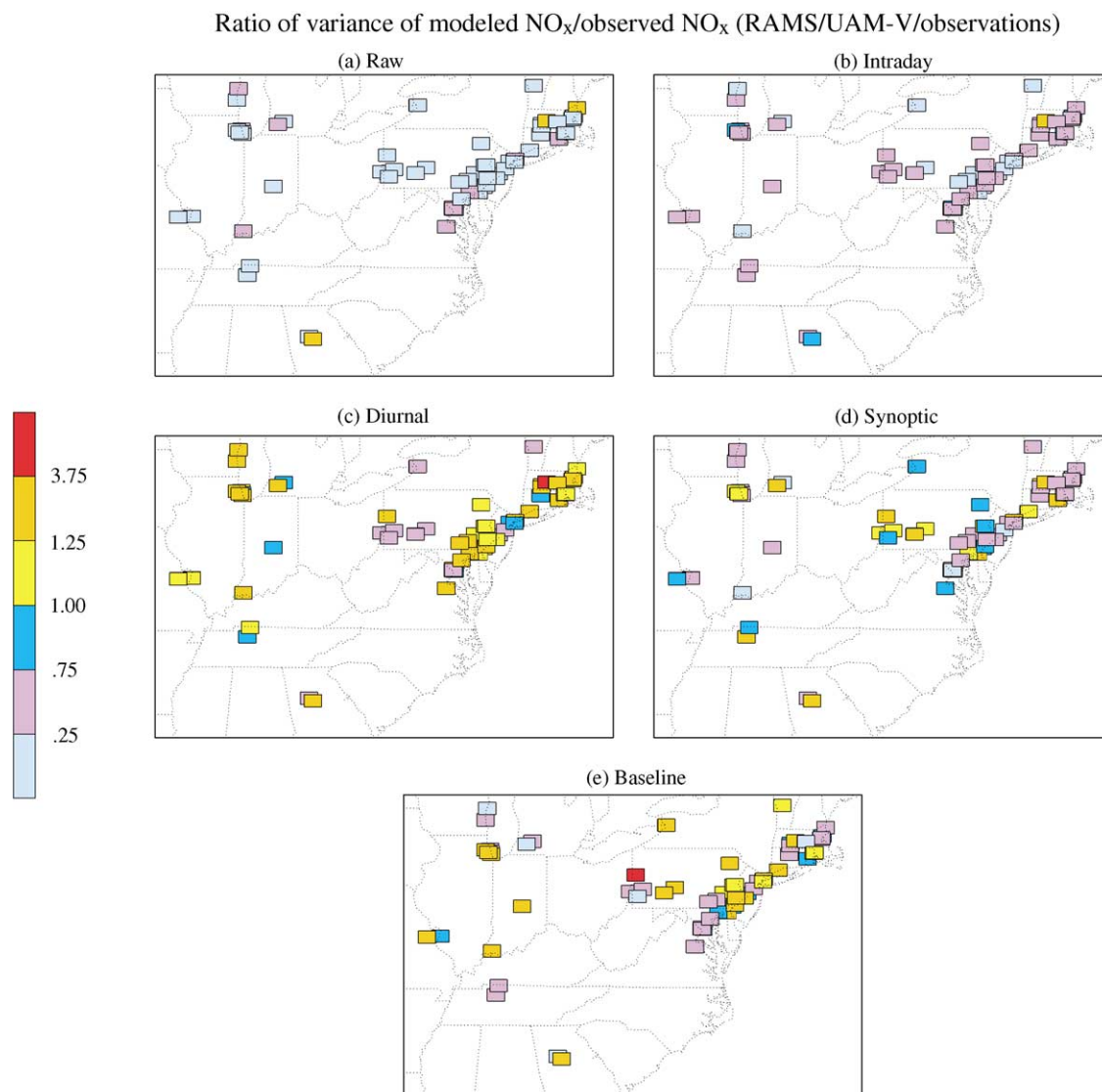


Fig. 5. Ratio of modeled to observed variances of NO_x in RAMS/UAM-V for different time scales.

To address the question whether the modeled NO_x concentrations capture the observed pattern in terms of the relative strength of forcing on different time scales, the contribution of each filtered component to the total variance is computed. The results for the data at the Harvard Forest site are shown in Fig. 7. The prominent variability in both model predictions and observations occurs on the diurnal scale, and is related to the time scale for the variability in anthropogenic and biogenic emissions as well as differences between daytime and nighttime chemistry. This is consistent with the results obtained from the power spectrum of NO_x observations at Harvard Forest, which shows most energy on the diurnal scale. Both models place much higher emphasis

on the diurnal scale at this site with 68% of the variability in NO_x in RAMS/UAM-V, and 70% of the variability in NO_x in MM5/MAQSIP compared to approximately 46% in the observations attributable to the diurnal forcing. The synoptic component is the next highest contributor in the observations. Both modeling systems underestimate the synoptic forcing, with RAMS/UAM-V predicting a relative contribution of 10% to the total variance (Fig. 7b) and MM5/MAQSIP predicting a relative contribution of 21% to the total variance (Fig. 7c). The analysis is repeated after classifying the sites into rural and urban (suburban inclusive) environments. The diurnal forcing is relatively the strongest of all the components in both rural and

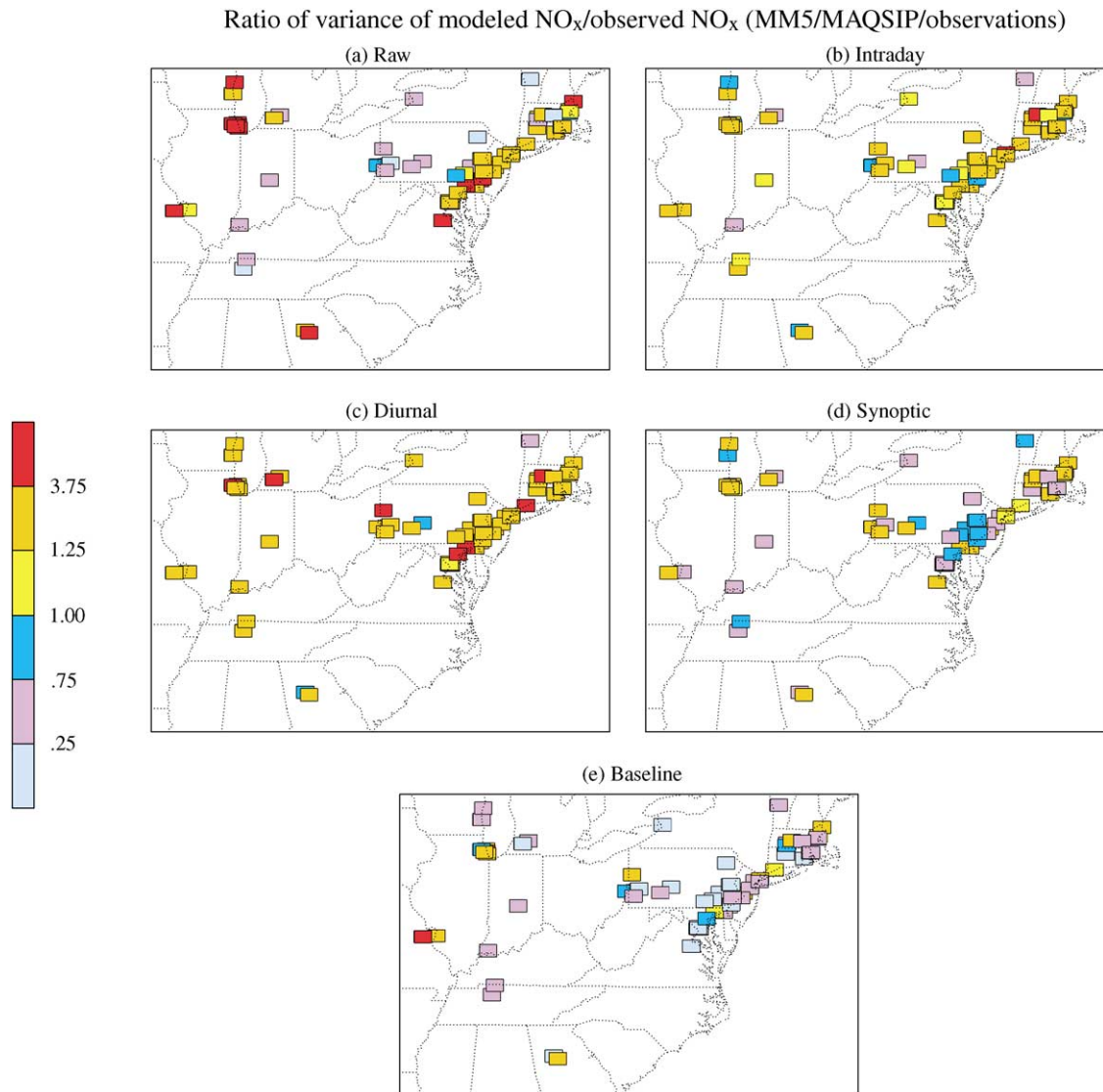


Fig. 6. Same as Fig. (5) except for NO_x from MM5/MAQSIP.

urban environments. The modeled diurnal forcing is about 10% lower at rural sites than at urban sites in both modeling systems (not shown). The baseline contribution is seen to be higher for the rural sites in both observations and model predictions (not shown). Both model predictions and observations have greater variance on the synoptic and baseline scales at the rural sites than at the urban sites, indicating the importance of transport and longer-term processes at rural locations.

To examine the behavior of the diurnal component in more detail, the average diurnal cycle (Fig. 8a) and the average rate of change in the diurnal component (Fig. 8b) were plotted for the Morrisania Center site in New York City (AIRS-ID 360050080) for the observations and predictions from the two modeling systems.

From Fig. 8a, it is evident that both amplitude and phase of the average diurnal cycle in the models are different from the observations. The MM5/MAQSIP system overestimates the diurnal amplitude by a larger amount than RAMS/UAM-V, which leads to the overestimation of variances of diurnal forcing at most of the sites (Fig. 6c). Both modeling systems overestimate the rate of change in the early morning hours (Fig. 8b). The early morning processes affecting NO_x include fresh emissions and vertical mixing as boundary layer begins to grow. The late morning processes are dominated by boundary-layer growth and photochemical production of ozone from NO_x and the late afternoon processes are dominated by removal of NO_x in the form of HNO₃ and boundary layer decay. The

Relative contribution to variance at Harvard Forest

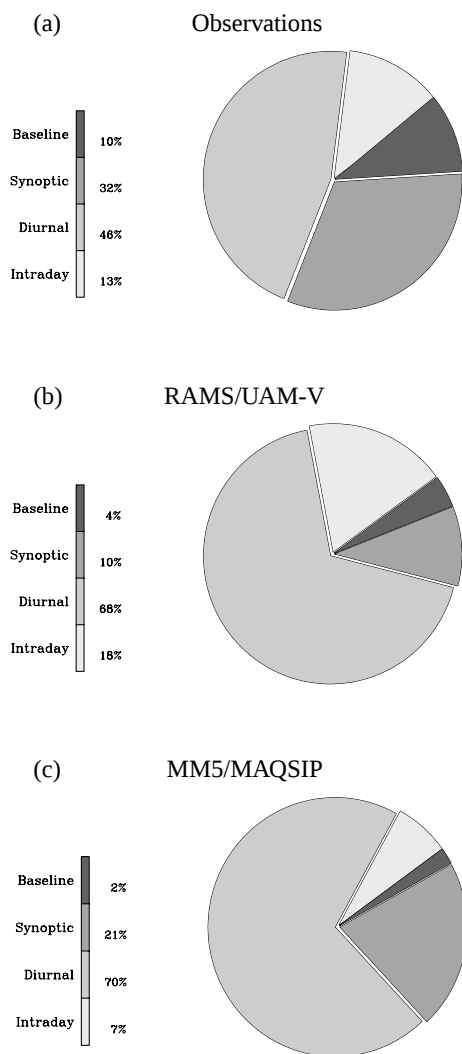


Fig. 7. Relative contribution of the four temporal components to the total variance of NO_x data from the Harvard Forest site in Central Massachusetts from (a) observations, and (b) model outputs.

results suggest that the modeling systems do not capture the contribution of these dynamical processes to the diurnal cycle properly; the RAMS/UAM-V system appears to capture the diurnal variations of NO_x better than the MM5/MAQSIP system at this site.

Spatial correlations for the different temporal components of NO_x from all possible pairs of sites are also computed to study the spatial differences in the behavior of model predictions and observations of NO_x (Fig. 9). The results for the intra-day component show that the correlations between pairs of sites in model outputs are significantly higher than those in observations. While the

correlations for the intra-day component in the observations drop off rapidly with distance (to 0.25 within a distance of 10 km), both models continue to show high of spatial correlation on this time scale (Fig. 9a). The diurnal and synoptic components (Figs. 9b and c, respectively) are better represented in the model while there is a significant disparity between the observations and model predictions for the baseline component (Fig. 9d). Both models captured the variability better for ozone than for precursors on the diurnal, synoptic, and baseline scales (see Hogrefe et al., 2001b). However, even for ozone, the observed variability on the intra-day scale is not well-simulated by the two modeling systems (Hogrefe et al., 2001b).

In the following, we attempt to explain some of the results described above in terms of the chemical and physical forcings prescribed in the photochemical model. Specifically, we discuss the impact of emissions, temperature and vertical mixing on the simulated NO_x concentrations. Looking at the temporal variation of domain-wide total daily emissions presented in Houyoux et al. (2000), for anthropogenic NO_x emissions the largest contributor (around 50%) are point sources which exhibit almost no seasonality and a moderate weekly cycle. The next largest category is mobile with no evident seasonality and a bigger weekly cycle and some intra-week variability because of temperature adjustment of mobile sources. The last category is area sources with no seasonal variation, a very pronounced weekday/weekend cycle and no intra-week variability. In addition, anthropogenic NO_x sources show strong diurnal variability. Biogenic NO_x shows a very small seasonal cycle (higher emissions later in the summer) due to influence of temperature and solar radiation (Houyoux et al., 2000), but this variation is very small compared to other sources. Overall, looking at the temporal variability of total NO_x emissions, we notice a pronounced diurnal variability in the emissions and a pronounced weekday/weekend cycle in both modeling systems. There is also some seasonal variability in case of biogenic NO_x emissions, which could affect the baseline component of NO_x, but this variation is not very conspicuous. Overall, the most pronounced variability in NO_x emissions is on the diurnal scale, which could explain the strong diurnal variance of NO_x in both modeling systems; the differences the emission inventories used in the two modeling systems are not very significant.

Differences in meteorological inputs can lead to differences in the predicted pollutant concentrations by the photochemical models (Biswas and Rao, 2001). Sillman and Samson (1995) found that ozone concentrations increases with temperature, and Alapaty et al. (1995) found that modeled ozone concentrations can differ as much by ± 90 ppb at individual grid cells even when there is a systematic bias in the temperature and mixing heights. A detailed analysis of spectral

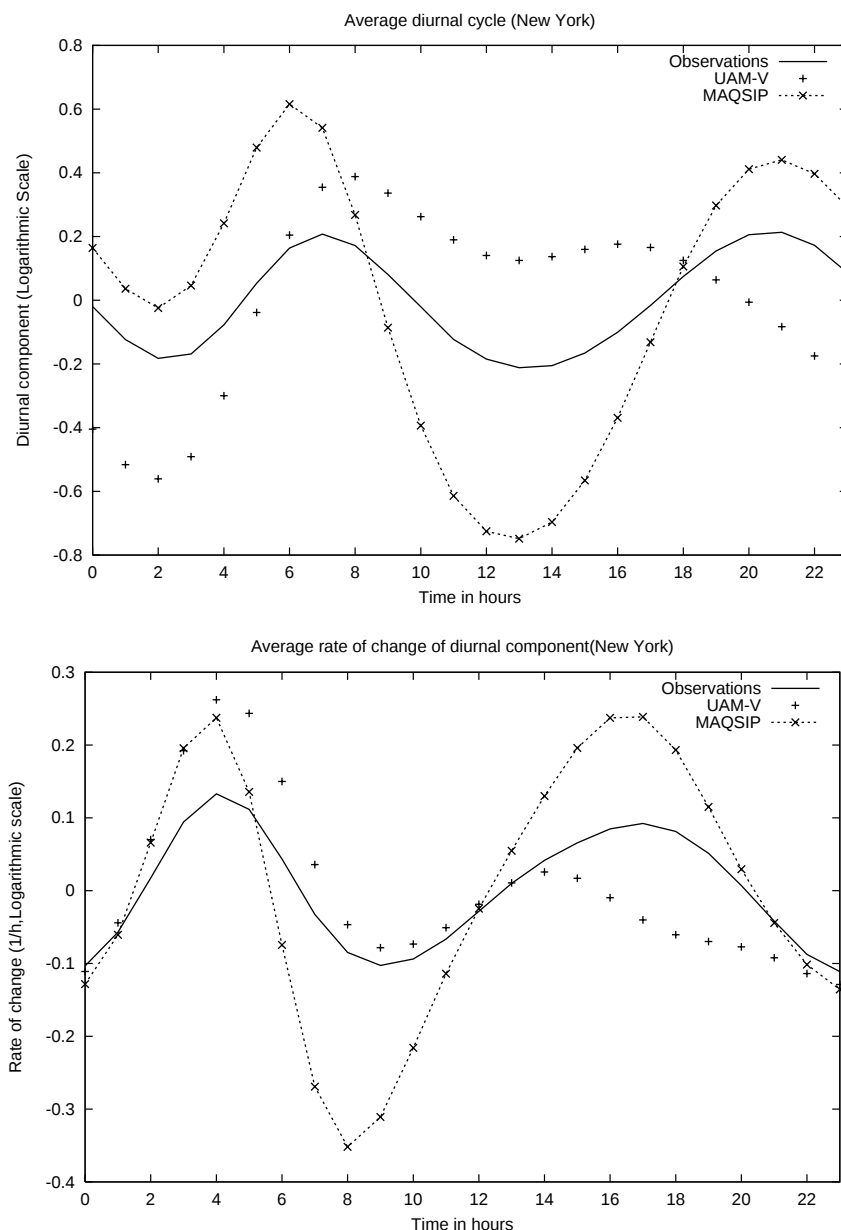


Fig. 8. (a) Average diurnal cycle and (b) average rate of change of diurnal component for NO_x at an AIRS site in New York.

decomposition of the meteorological variables of RAMS and MM5 was done in Part I of this series of papers (Hogrefe et al., 2001a). In the case of temperature, both RAMS and MM5 and observations displayed the highest variance on the diurnal scale followed by the baseline component and the synoptic forcing. Overall, the RAMS meteorological model displayed higher temperatures than MM5 meteorological model since RAMS was run in the dry mode (absence of clouds). Though higher temperatures enable greater mixing of

pollutants which should mean lower variance especially on the diurnal scale, it is difficult to quantify the exact impact of temperature because of the influences of other meteorological variables.

The vertical diffusivity in RAMS is computed from the vertical distribution of the turbulent kinetic energy (TKE) and the MM5 diffusivity is diagnosed based on eddy-diffusion (K theory). Details regarding the computation of vertical diffusivity using these methods can be found in Pleim and Chang (1992) and Alapaty et al.

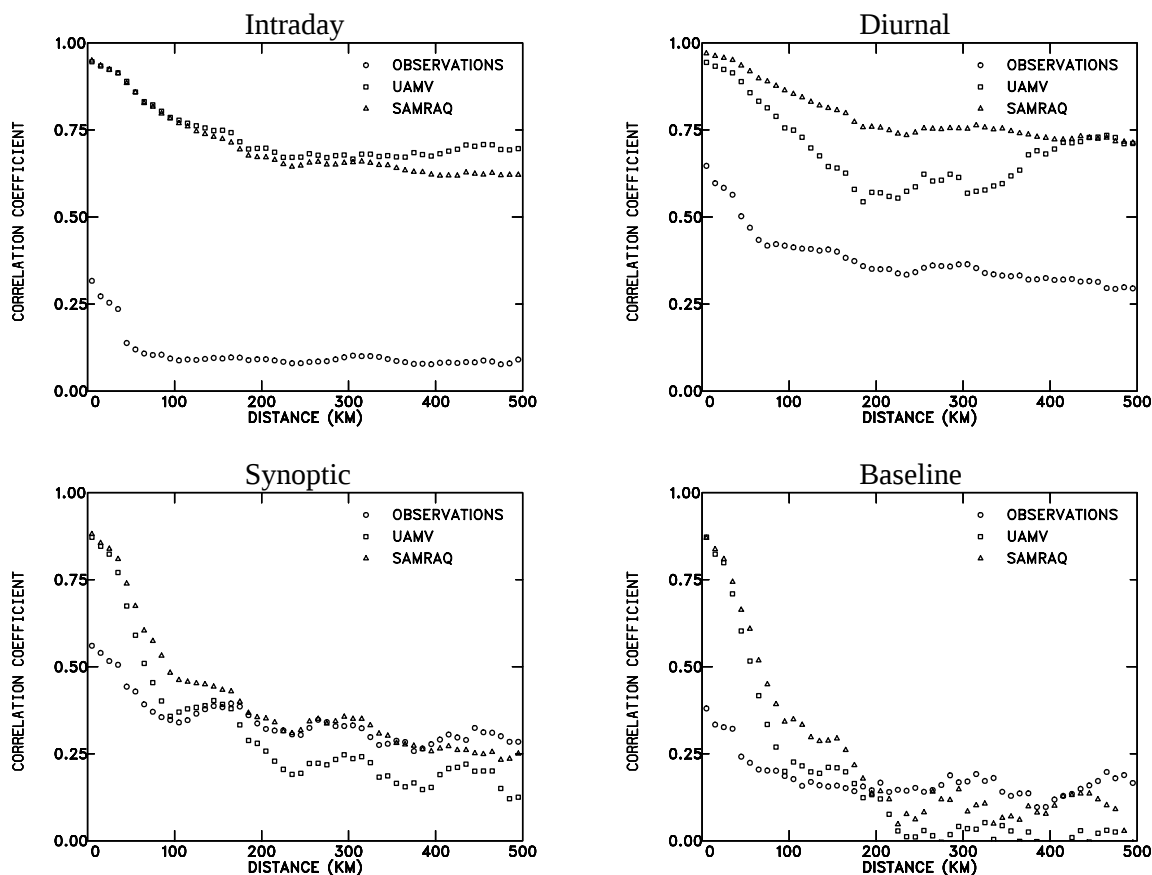
Plot of NO_x correlations with distance

Fig. 9. Correlation coefficient as a function of distance (km) for all pairs of sites from observations and model predictions for NO_x on different time scales.

(1997). Nowaki et al. (1996) and Imhoff et al. (2000) demonstrated that vertical diffusivity computed by different methods can be significantly different and may potentially be a source of large uncertainty in photochemical modeling. Nowaki et al. (1996) found that reactive chemical species were more sensitive to vertical diffusion values. Both UAM-V and MAQSIP rely on vertical diffusivities to determine their vertical mixing. Hence, differences in the estimation of mixing depths between the two modeling systems lead to differences in precursor predictions.

The photochemical lifetime of NO_x is on the order of several hours from inception to its removal in the form of HNO₃. The lifetime of HNO₃ is affected by dry deposition ($\sim 2.5\% \text{ h}^{-1}$ during the day), but much lower at night due to stratified stable layers. It is removed by wet deposition during the night and reaction with NH₃ forming particulates. This reaction is temperature-dependent. The higher the temperatures, the greater are the removal rates for HNO₃. The impact on NO_x

due to chemistry is mostly in the intra-day and diurnal time scales. But, since both the modeling systems incorporate the same CB-IV bond mechanism, the effects due to chemistry on both modeling systems are similar except for the temperature dependence of the reaction rates. The higher temperatures in RAMS could accelerate the removal process of NO_x, creating a lower diurnal variance at most of the sites in the RAMS/UAM-V system compared to the MM5/MAQSIP system.

3.2. Observed and modeled NO_y

NO_y represents the sum of all reactive oxidized nitrogen species and is a surrogate species being used to represent the various groups of nitrogen oxides involved in ozone photochemistry (Olszyna et al., 1994). NO_y has also been used as an indicator species for NO_x-VOC sensitivity (Milford et al., 1994; Sillman, 1995). In rural environments, NO_y is primarily composed of NO,

NO₂, peroxyacetyl nitrate (PAN), HNO₃ and aerosol NO₃⁻ (Fahey et al., 1986). All four sites with available NO_y data in this study (Arentsville, PA—ARE, Kunkletown, PA—KUN, Brookhaven, NY—BNL, and Harvard Forest, MA—HF) are in non-urban environments (see Fig. 1b). The modeled mean NO_y concentration is higher than the measured level at each site except at Brookhaven, New York (BNL) for RAMS/UAM-V (not shown). MM5/MAQSIP predicted higher mean NO_y concentrations than observed and that of RAMS/UAM-V at all the four sites (not shown).

The correlation coefficients and the ratio of the modeled to observed variances of NO_y are presented in Table 2a and b, respectively. The intra-day components of the modeled values and observations are poorly correlated, consistent with the results for NO_x. The strongest relationship between modeled and observed values of NO_y is seen for the synoptic component, followed by the baseline and the diurnal components in both models. The ratios of the variances for the raw (unfiltered) data show that the model estimates of the variance of NO_y are higher at all sites except Arentsville, Pennsylvania in the case of RAMS/UAM-V predictions and observations. However, as found earlier for NO_x, both models under-represent the variance of NO_y on the intra-day scale. The variance of the modeled values for the other temporal components is generally higher than the measurements. The variance in the unfiltered (raw) data from MM5/MAQSIP is significantly higher than that of the observations (Table 2b). A major contributor towards these high ratios is the diurnal component which is overestimated at all sites

except at Brookhaven, New York. The higher diurnal variances are again caused by the higher diurnal amplitudes in both modeling systems (not shown).

The relative contributions of the temporal components to the total variance of NO_y at Harvard Forest are presented in Table 2c. The results show that 50% of the variability in the observations of NO_y concentrations is forced by the synoptic-scale processes at this site. The model estimates of the energy associated with the synoptic component is lower than in the observations; the synoptic component of NO_y in RAMS/UAM-V is 29% and is 40% in MM5/MAQSIP. In the observations, the baseline component is the next highest contributor followed by the diurnal component. In both modeling systems, the diurnal component contributes significantly to NO_y variability (56% in RAMS/UAM-V and 50% in MM5/MAQSIP). Both modeling systems underestimate the variance on the baseline time scale.

3.3. Observed and modeled VOC

As noted before, both RAMS/UAM-V and MM5/MAQSIP incorporate the Carbon Bond mechanism IV (CBM-IV) (Gery et al., 1989). The composition of total VOC concentrations in the observations (PAMS data sites) is different from the treatment of VOC concentrations in the CBM-IV mechanism. In the CBM-IV mechanism, most hydrocarbon classes consist of a mixture of different individual hydrocarbons. Therefore, to compare the observations with model predictions, we have chosen four VOC classes that are relatively “pure” (i.e. the contribution of other hydrocarbons towards

Table 2

Sites	Coefficient of correlation					Ratio of variance (modeled/observed)				
	Raw	ID	DI	SY	BL	Raw	ID	DI	SY	BL
(a) (RAMS/UAMV vs. observations)—NO _y										
ARE	0.33	0.06	0.19	0.64	0.51	0.91	0.33	1.92	0.88	0.29
KUN	0.47	0.07	0.26	0.81	0.71	3.23	0.56	1.78	2.08	1.02
BNL	0.49	0.21	0.47	0.68	0.51	1.16	0.43	1.15	1.78	3.21
HF	0.59	0.09	0.32	0.74	0.45	1.33	0.42	0.77	0.94	0.57
(b) (MM5/MAQSIP vs. observations)—NO _y										
ARE	0.23	0.03	0.02	0.67	0.24	4.40	0.85	4.08	0.99	0.25
KUN	0.35	0.17	0.29	0.77	0.82	9.60	0.66	2.44	0.99	0.61
BNL	0.43	0.26	0.49	0.67	0.21	2.10	0.35	0.87	1.20	2.69
HF	0.56	0.07	0.44	0.82	0.42	3.21	0.72	1.77	0.75	0.42
(c) Relative contribution to variance at Harvard Forest (%)—NO _y										
	Intraday	Diurnal	Synoptic	Baseline						
Observations	3	20	50	27						
RAMS/UAM-V	2	57	29	12						
MM5/MAQSIP	2	51	40	7						

their concentrations in the CBM-IV mechanism is negligible). The four VOC species chosen here are (a) ethene, (b) isoprene, (c) toluene, and (d) xylene. While two of these compounds chosen (ethene and isoprene) are “pure” in the CBM-IV mechanism, xylene and toluene have other species, besides themselves, to contribute to their carbon bond mechanism, though the contribution towards their concentrations by other hydrocarbons is relatively small. In terms of concentrations, isoprene, toluene and xylene make up a significant portion of the total VOCs, though this contribution can vary from site to site. In addition, these four species have significant ozone forming potential. (ozone formed/g-VOC emitted) (Carter et al., 1993).

Some of the other VOC species may have higher ozone forming potential, but their concentrations are “hybrid” consisting of significant concentrations of other hydrocarbons as well, causing difficulties in comparing observations with model-predicted values. Since isoprene is primarily of biogenic origin and also has a high reactivity, it is an important contributor to ozone formation. The assumption behind ozone-forming potential or reactivity is that in addition to specific concentrations of VOCs emitted in a given region, the difference in the chemistry of each of the VOCs has to be considered while assessing their impact on ozone formation (NRC, 1999). The VOCs differ greatly from each other in their reactivity and in their potential for forming tropospheric ozone. The more reactive a given species is, the greater is its impact on tropospheric ozone formation. The VOCs are oxidized by their reaction with

hydroxyl (OH) radicals and the faster the reaction rate, the more reactive is that particular species of VOC (NRC, 1999). The reactivity scale, also referred to as the OH-reactivity or the k_{OH} , expresses the relative contributions of VOCs in terms of their rate constants with OH (Chameides et al., 1992). The unit of k_{OH} is $\text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}$. The maximum incremental reactivity (MIR) scale is a quantitative measure of ozone-forming potential (NRC, 1999). Ethene has a k_{OH} of 8.5 and a MIR of 8.3 (NRC, 1999). Isoprene has a k_{OH} of 101 and a MIR of 9.3 (NRC, 1999). Toluene has a k_{OH} of 6.0 and a MIR of 5.1, whereas *m*-xylene has a k_{OH} of 24 and a MIR of 14.2 (NRC, 1999). Ethene, toluene and xylene have lifetimes on the order of few hours and are emitted mostly from motor vehicles. They react near their sources and can contribute to the photochemical production of ozone near the regions where they are emitted.

The results for the correlations between modeled and observed isoprene for different temporal components, and the ratio of their variances, are listed in Table 3 for 8 sites in the northeastern United States. The results from RAMS/UAM-V and observations are shown in Table 3a, while the results from MM5/MAQSIP and observations are shown in Table 3b. The eight sites chosen here for the analysis are McCauliffe Park, Connecticut (AIRS ID 110010043), Lums Pond, Delaware (AIRS ID 100030018), McMillan Reservoir, Washington DC (AIRS ID 110010043), Cape Elizabeth, Maine (AIRS ID 230052001), Lynn, Massachusetts (AIRS ID 250092006), Chicopee, Massachusetts (AIRS ID

Table 3

Sites	Correlation coefficients					Ratio of variances (modeled/observed)				
	Raw	ID	DI	SY	BL	Raw	ID	DI	SY	BL
(a) (RAMS/UAM-V vs. observations)—Isoprene										
090031003	0.47	0.11	0.29	0.60	0.92	1.8	2.1	4.6	0.75	0.72
100030018	0.11	−0.01	0.08	0.11	0.63	4.3	1.9	3.7	1.5	0.87
110010043	0.04	−0.05	−0.08	0.34	0.05	1.8	1.54	11	3.8	1.7
230052001	0.18	0.006	−0.2	0.52	0.50	0.99	3.97	2.9	1.7	0.6
250092006	0.06	−0.02	−0.3	0.40	0.83	0.80	4.0	1.2	2.6	1.9
250130008	0.02	−0.01	−0.3	0.37	0.62	0.34	1.1	1.4	0.38	0.4
340210005	0.08	0.004	−0.08	0.002	0.67	0.52	3.3	1.3	1.5	1.1
360050083	0.27	−0.07	−0.32	0.15	0.83	1.3	7.2	9.4	3.6	1.9
(b) (MM5/MAQSIP vs. observations)—Isoprene										
090031003	0.37	0.04	0.27	0.39	0.55	11.1	2.7	7.7	1.91	0.37
100030018	0.55	0.36	0.56	0.084	0.27	6.7	1.7	3.8	2.5	0.29
110010043	0.37	0.14	0.25	0.40	0.47	3.1	1.4	4.7	3.2	0.20
230052001	0.38	0.19	0.39	0.70	0.03	3.2	0.98	3.6	3.0	1.3
250092006	0.39	0.38	0.66	0.75	0.58	3.1	1.5	1.1	2.6	1.1
250130008	0.40	0.18	0.53	0.54	0.25	1.8	1.5	1.9	1.1	0.66
340210005	0.52	0.43	0.68	0.53	0.73	3.8	1.1	0.1	1.4	1.0
360050083	0.27	−0.07	0.32	0.15	0.83	3.4	0.99	2.0	2.0	0.9

250130008) and Rider College, New Jersey (AIRS ID 340210005). The results show that both modeling systems exhibit higher correlations on the baseline scale followed by the diurnal and synoptic time scales. The MM5/MAQSIP system shows higher correlations with observations on the diurnal scale compared to the RAMS/UAM-V system, suggesting that it is capturing the diurnal variation better than the RAMS/UAM-V. Both modeling systems exhibit low correlations on the intra-day scale. These results reveal that the observed variability on the longer time scales are better represented than the variability on shorter time scales in both modeling systems. Since isoprene emissions are strongly temperature dependent, this result is consistent with the finding in Part I of this series (Hogrefe et al., 2001a) which showed that correlations between the observed and predicted temperature fluctuations were highest on the baseline time scale.

The results of the ratios of variances of modeled and observed values of isoprene reveal that RAMS/UAM-V overpredicts the variance at some sites and underpredicts the variances at some other sites (Table 3a). MM5/MAQSIP overpredicts the variance at all sites (Table 3b). Looking at the ratio of variances in the raw (unfiltered) isoprene data, the RAMS/UAM-V system is closer to the observed variance than the MM5/MAQSIP system. The ratios of variances between models and observations are higher on the intra-day and diurnal scales than those on the synoptic and baseline scales.

The relative contributions to the total variance in the models and observations for each of the four VOC species of interest are computed at the PAMS data site in Bronx, New York City. For ethene, the results show that the diurnal component is the largest contributor, followed by the synoptic component in both modeling systems and observations though the actual magnitudes vary in the observations and the models (Table 4a). In the observations, the relative contribution to the total variance is higher on the intra-day component (14%) than on the baseline component (8%). The MM5/MAQSIP system shows 15% on the intra-day scale and 4% on the baseline scale and is in closer agreement with the observations than RAMS/UAM-V which shows 4% and 21% contribution on the intra-day and baseline time scales, respectively.

The results for isoprene in Table 4b indicate that the diurnal component is the highest contributor towards the relative variance, followed by the synoptic component, in both modeling systems and in observations. Both modeling systems underestimate the baseline component of the variance and overestimate the contribution of the intra-day variance. For toluene (Table 4c) and xylene (Table 4d), the amplitude of fluctuations is seen to be greatest in the diurnal component, followed by synoptic, baseline and intra-day components in both models and in observations. It

Table 4
Relative contribution to variance at Bronx (%)

	Intraday	Diurnal	Synoptic	Baseline
(a) <i>Ethene</i>				
Observations	14	43	35	8
RAMS/UAM-V	4	56	19	21
MM5/MAQSIP	11	57	25	7
(b) <i>Isoprene</i>				
Observations	17	47	19	17
RAMS/UAM-V	28	35	30	7
MM5/MAQSIP	25	50	19	6
(c) <i>Toluene</i>				
Observations	12	31	36	22
RAMS/UAM-V	3	64	21	11
MM5/MAQSIP	10	51	29	11
(d) <i>Xylene</i>				
Observations	23	46	23	8
RAMS/UAM-V	9	63	16	12
MM5/MAQSIP	15	55	25	4

is also evident that the modeled values for toluene exhibit significantly lower variance than the observed data on the baseline time scale (Table 4c). In the case of xylene, the RAMS/UAM-V system overestimates the baseline component while the MM5/MAQSIP system underestimates the baseline with respect to observations (Table 4d). On the synoptic-scale, for both xylene and toluene, MM5/MAQSIP captured the magnitude of the synoptic-scale contribution to the total variance better than RAMS/UAM-V.

The decay in the correlations as a function of distance is also computed for isoprene (not shown). The results reveal that, on the on the intra-day scale, the models maintain a significant amount of spatial correlation with distance, whereas in the observations, the correlation coefficient rapidly decreases to 0.25 within a distance of 20–30 km. On the diurnal scale, both modeling systems show higher correlations with distance whereas in the observations, the correlations drop to 0.5 within a distance of 10 km. Hence, both modeling systems fail to reproduce the observed spatial variability on both intra-day and diurnal scales. Both modeling systems best capture the observed fluctuations on the synoptic-scale. On the baseline scale, there is not much agreement between observations and model predictions. The patterns of spatial correlations are similar to other hydrocarbon species like ethene, xylene and toluene (not shown).

Previous studies have shown that the VOC/NO_x ratio plays a key role in determining the rate of formation and sensitivity of ozone to emissions of VOC and NO_x (Lin et al., 1988; McKeen et al., 1991). Ozone production

over most of the eastern US has been shown to be NO_x -limited (McKeen et al., 1991). Isoprene/ NO_x ratios for morning hours of the summer of 1995 for the model predictions and observations are presented at the Harvard Forest site in Fig. 10. The shaded periods indicate the three high ozone episodes that occurred during the summer of 1995. In the observations, the peaks are not sharply defined for the episodic days vs. non-episodic days (Fig. 10a). The RAMS/UAM-V system exhibits distinctly higher isoprene/ NO_x ratio on episodic days compared to non-episodic days (Fig. 10b). Two of the three episodes exhibit sharper peaks in case of the RAMS/UAM-V system. The MM5/MAQSIP system shows lower isoprene/ NO_x ratio than the observations and the RAMS/UAM-V system, but displays slightly sharper peaks on episodic days compared to non-episodic days (Fig. 10c). Additional peaks occur over the season in both observations and model predictions, with those in the observations being greater than the model estimates.

3.4. Precursor forcings during ozone episodes

To further examine the differences in the dynamical forcings of the precursor concentrations over the entire season and over the days when ozone concentrations exceed 100 ppb (ozone episodes), the distribution of hourly NO_x concentrations are constructed from the observations (Fig. 11) and the two modeling systems (Figs. 12 and 13) on different time scales. The results reveal that the intra-day component has almost the same distribution over the season as over high ozone days in observations and model predictions. The diurnal forcing is slightly different in the two distributions for each case. However, the synoptic and baseline components clearly show that high ozone events are associated with stronger than average NO_x forcing on these time scales (see Figs. 11–13), indicating the importance of longer time scales to ozone exceedance events. Thus, as evident in the observations and the two modeling systems, during a typical episode day, the elevated levels of ozone are related to the positive forcings on the baseline and synoptic time scales of precursor concentrations. The models seem to reproduce the characteristics of the observations reasonably well in this case.

Hogrefe et al. (2000) showed that the processes occurring on time scales greater than 1 day are the essential forcing mechanisms for elevated ozone levels. Their results indicated that the three major ozone episodes that occurred during the summer of 1995 were associated with elevated levels of the baseline and reinforced by the strong positive synoptic forcing. The results from the analysis of precursor data also reveal that the longer-term components play a significant role in determining the precursor variability and in dictating ozone episodes.

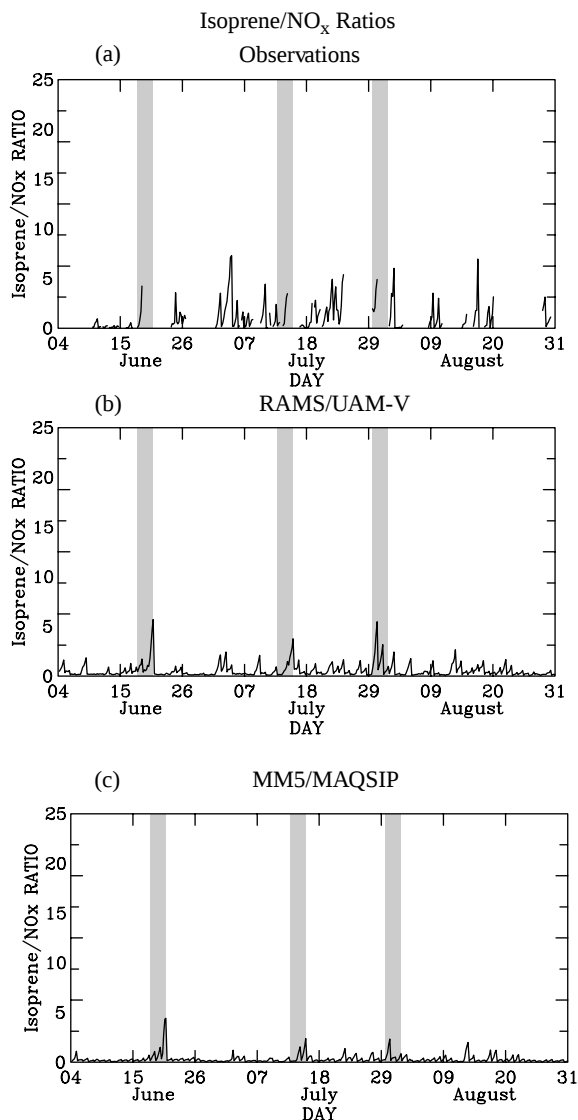


Fig. 10. Time series of morning (6–10 am EST) ratios of isoprene/ NO_x : (a) observations, (b) RAMS/UAM-V system, and (c) MM5/MAQSIP system.

4. Summary

Hourly NO_x , NO_y and VOC data from observations and model simulations for the period 4 June–31 August 1995 were examined to assess model performance for ozone precursors on different time scales; analyses on the resolvable time scales, namely, intra-day, diurnal, synoptic and baseline time scales have been performed. The observations show that the prominent variability of NO_x occurs on the diurnal scale. While the highest contribution to the total variance in the modeled NO_x is also found on the diurnal scale, both RAMS/UAM-V

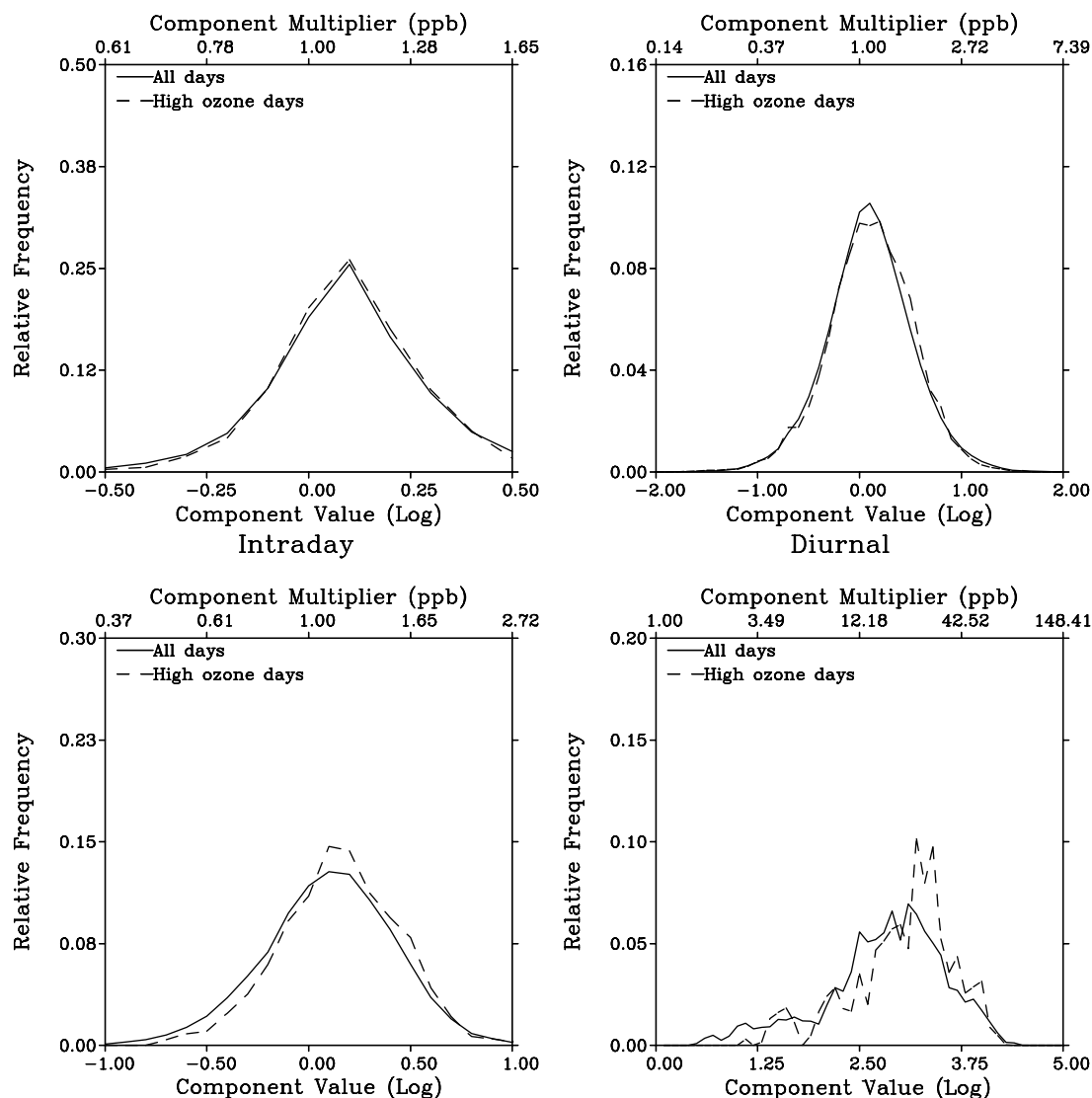
NO_x DISTRIBUTION FROM OBSERVATIONS

Fig. 11. Distribution of hourly NO_x from observations over the entire season (solid lines) and over the days when measured ozone levels exceeded 100 ppb.

and MM5/MAQSIP overestimate the strength of the diurnal forcing when compared to the observations. The results for the correlations between the observed and modeled NO_x indicate that model performance is best representative of the observations on the synoptic and baseline time scales while the observed and modeled NO_x are uncorrelated on the intra-day time scale. These poor correlations on the intra-day scale may be attributable in part to the horizontal grid dimension used in the model and the inability of the input meteorological and emissions fields to capture the

variations in time and space. This issue has been discussed for meteorological fields and ozone concentrations by Hogrefe et al. (2001a, b).

The major contribution to the total variance of observed NO_y stems from the synoptic component. Model simulations also show that the synoptic component is associated with the maximum variance for NO_y, though the relative contribution is higher in the model. The characteristics of the observed NO_y are better represented in the model for the longer time scales than for the intra-day component.

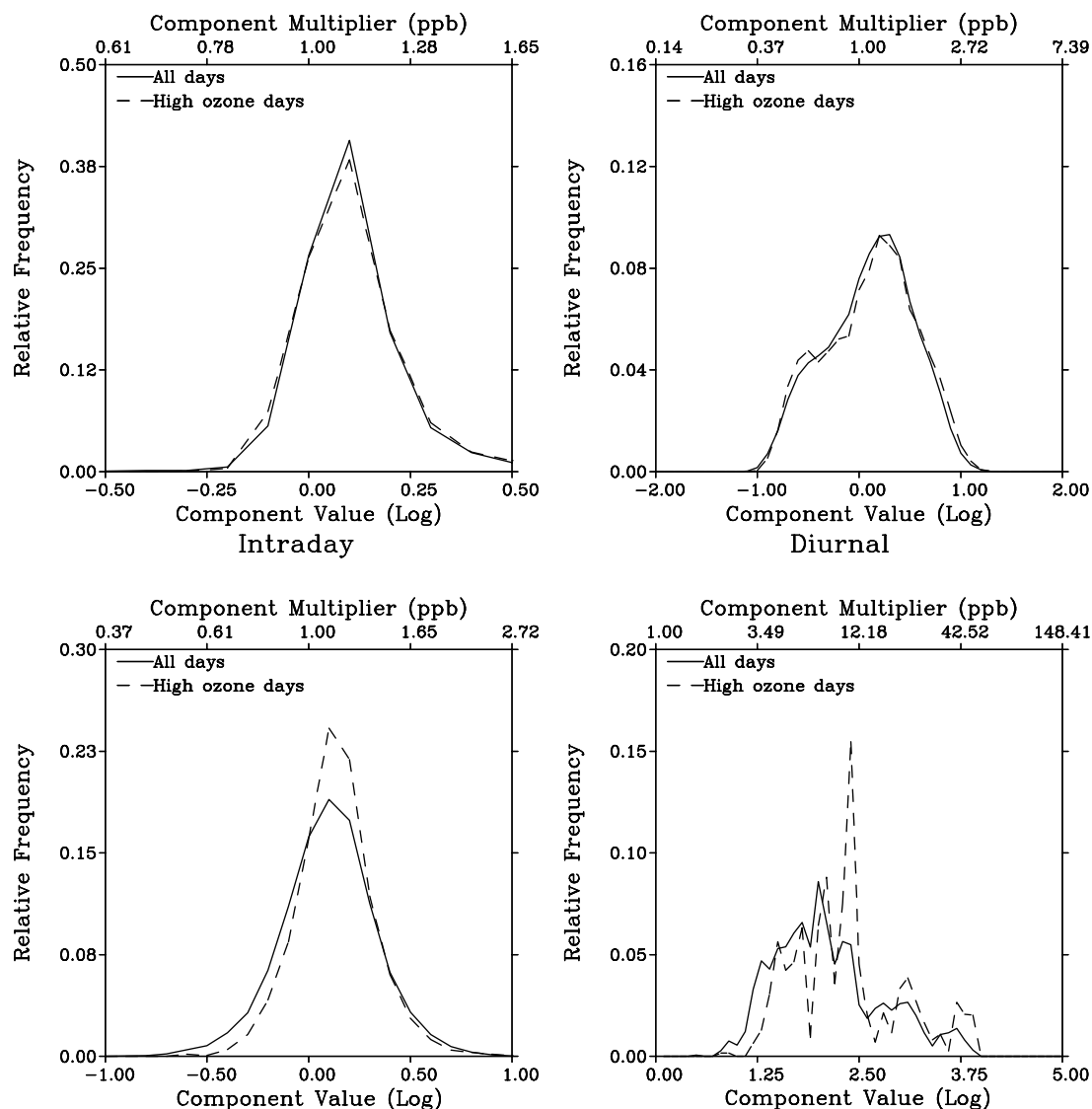
NO_x DISTRIBUTION FROM UAMV

Fig. 12. Distribution of hourly NO_x from RAMS/UAM-V over the entire season (solid lines) and over the days when measured ozone levels exceeded 100 ppb.

The diurnal and synoptic-scales are found to be most influential in determining the variance of VOC in observations and model simulations. The baseline component contributes significantly to the total variance in the observed data. Both modeling systems underestimate the variability in the intra-day component and the baseline components. The results suggest that the longer-term forcings for the precursor concentrations are relatively better represented than the short-term forcings in the model. The intra-day fluctuations are not

well-captured by the two models with the current grid dimension.

The above results indicate that the longer-term forcings play a relatively larger role in determining the precursor variability, and, consequently, elevated levels of ozone than the intra-day fluctuations. Thus, to successfully model ozone episodes, photochemical model simulations must cover longer time periods with proper representation of the processes occurring on longer time and space scales.

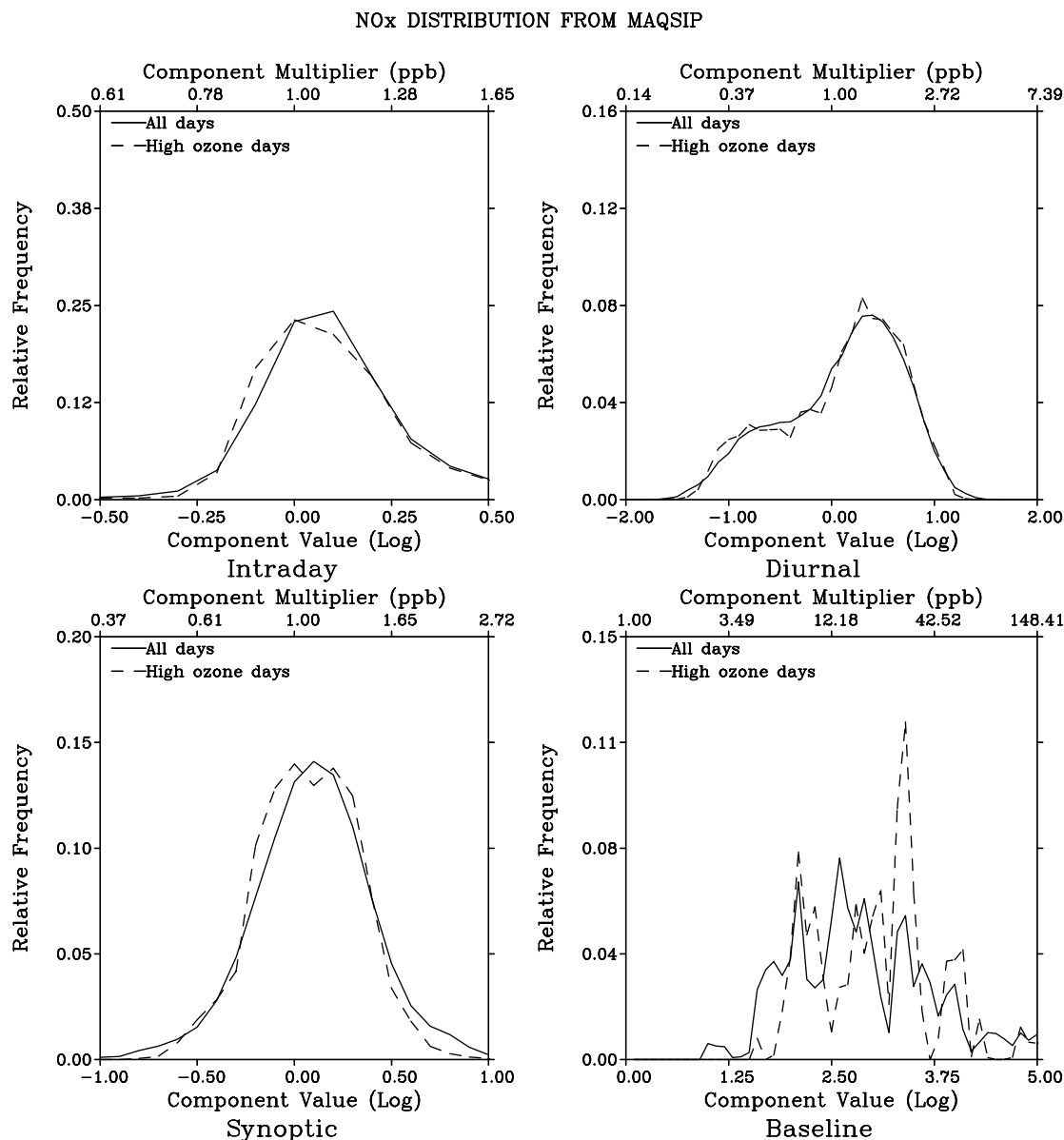


Fig. 13. Distribution of hourly NO_x from MM5/MAQSIP over the entire season (solid lines) and over the days when measured ozone levels exceeded 100 ppb.

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References

- Alapaty, K., Olerud Jr., D.T., Schere, K.L., Hanna, A.F., 1995. Sensitivity of regional oxidant model predictions to prognostic and diagnostic meteorological fields. *Journal of Applied Meteorology* 34, 1787–1795.
- Alapaty, K., Pleim, J.E., Raman, S., Niyogi, D.S., Byun, D.W., 1997. Simulation of atmospheric boundary layer processes using local and nonlocal-closure schemes. *Journal of Applied Meteorology* 36, 214–233.
- Biswas, J., Rao, S.T., 2001. Uncertainties in episodic ozone modeling stemming from uncertainties in the meteorological fields. *Journal of Applied Meteorology* 40, 117–135.
- Carter, W.P.L., Pierce, J.A., Malkina, L., Luo, D., Long, W.D., 1993. Environmental Chamber Studies of Maximum Reactivities of Volatile Organic Compounds. Report to Coordinating Research Council, Project No. ME-9; California, Air Resources Board, Contract No. A032-0692; South Coast Air Quality Management District, Contract No. C91323; United States Environmental Protection Agency, Cooperative Agreement No. CR-814396-01-0; University Corporation for Atmospheric Research, Contract No. 59166; and Dow Corning Corporation, 1 April.
- Chameides, W.L., Lindsay, R.W., Richardson, J., Kiang, C.S., 1988. The roles of biogenic hydrocarbons in urban photochemical smog: Atlanta as a case study. *Science* 241, 1473–1475.
- Chameides, W.L., Fehsenfeld, F.C., Rodgers, M.O., Cardelino, C., Martinez, J., Parrish, D.D., Lonneman, W., Lawson, D.R., Rasmussen, R.A., Zimmerman, P., Greenberg, J., Middleton, P., Wang, T., 1992. Ozone precursor relationships in ambient atmosphere. *Journal of Geophysical Research* 92, 14681–14700.
- Chameides, W.L., Saylor, R.D., Cowling, E.B., 1997. Ozone pollution in the rural US and the new NAAQS. *Science* 276, 916.
- Chang, J.S., Jin, S., Li, Y., Beauharnois, M., Lu, C.H., Huang, H.C., Tanrikulu, S., DaMassa, J., 1997. The SARMAP Air Quality Model, final report. Air Resources Board, California Environmental Protection Agency, Sacramento, CA.
- DiRienzo, A.G., Zurbenko, I.G., 1999. Semi-adaptive non-parametric spectral estimation. *Journal of Computer Graphics and Statistics* 8, 41–59.
- Eskridge, R.E., Ku, J.Y., Rao, S.T., Porter, P.S., Zurbenko, I.G., 1997. Separating different scales of motion in time series of meteorological variables. *Bulletin of the American Meteorological Society* 78, 1473–1483.
- Fahey, D.W., Hubler, G., Parish, D.D., Williams, E.J., Norton, R.B., Ridley, B.A., Singh, H.B., Liu, S.C., Fehsenfeld, F.C., 1986. Reactive nitrogen species in the troposphere: measurements of NO, NO₂, HNO₃, particulate nitrate, peroxyacetyl nitrate (PAN), O₃, and total reactive odd nitrogen (NO_x) at Niwot Ridge, Colorado. *Journal of Geophysical Research* 91, 9781–9793.
- Finlayson-Pitts, B.J., Pitts Jr., J.N., 1986. *Atmospheric chemistry: fundamentals and experimental techniques*. Wiley Interscience Publication, New York.
- Gery, M.W., Whitten, G.Z., Killus, J.P., Dodge, M.C., 1989. A photochemical kinetics mechanism for urban and regional scale computer modeling. *Journal of Geophysical Research* 94, 12925–12956.
- Grell, G.A., Dudhia, J., Stauffer, D., 1994. A description of the fifth-generation Penn State/NCAR Mesoscale Model (MM5). NCAR Technical Note, TN-398 + STR, National Center for Atmospheric Research, Boulder, CO, 138pp.
- Hogrefe, C., Rao, S.T., Zurbenko, I.G., Porter, P.S., 2000. Interpreting the information in ozone observations and model predictions relevant to regulatory policies in the Eastern United States. *Bulletin of the American Meteorological Society* 81, 2083–2106.
- Hogrefe, C., Rao, S.T., Kasibhatla, P., Kallos, G., Tremback, C.J., Hao, W., Olerud, D., Xiu, A., McHenry, J., Alapaty, K., 2001a. Evaluating the performance of regional-scale photochemical modeling systems: Part I—meteorological predictions. *Atmospheric Environment* 35, 4159–4174.
- Hogrefe, C., Rao, S.T., Kasibhatla, P., Hao, W., Sistla, G., Mathur, R., McHenry, J., 2001b. Evaluating the performance of regional-scale photochemical modeling systems: Part II—ozone predictions. *Atmospheric Environment* 35, 4175–4188.
- Houyoux, M.R., Coats Jr., C.J., Eyth, A., Lo, S., 1996. Emissions modeling for SMRAQ: a seasonal and regional example using SMOKE. *Proceedings of Computing in Environmental Resource Management*, 2–4 December. Air and Waste Management Association, Research Triangle Park, NC, pp. 555–566.
- Houyoux, M.R., Vukovich, J.M., Coats Jr., C.J., Wheeler, N.J.M., Kasibhatla, P., 2000. Emission inventory development and processing for the seasonal model for regional air quality. *Journal of Geophysical Research* 105, 9079–9090.
- Imhoff, R.E., Bailey, E.M., Mueller, S.F., 2000. The effect of vertical diffusivity on photochemical model estimates of tropospheric ozone. Preprints, 11th Joint Conference On the Applications of Air Pollution Meteorology with the A&WMA. American Meteorological Society, Long Beach, CA, pp. 116–120.
- Kasibhatla, P., Chameides, W.L., 2000. Seasonal modeling of regional ozone pollution in the eastern United States. *Geophysical Research Letter* 27, 1415–1418.
- Kasibhatla, P., Chameides, W.L., Duncan, B., Houyoux, M., Jang, C., Mathur, R., Odman, T., Xiu, A., 1997. Impact of inert organic nitrate formation on ground-level ozone in a regional air quality model using the carbon bond mechanism IV. *Geophysical Research Letter* 24, 3205–3208.
- Lagouvardos, K., Kallos, G., Kotroni, V., 1997. Modeling and analysis of ozone and its precursors in the northeast USA (Atmospheric modeling simulations). Final Report to Electric Power Research Institute, Paolo Alto, CA, 46pp [Available from Office of Science and Technology, NYS-DEC, 625 Broadway, Albany, NY 12233–3259].
- Lin, X., Trainer, M., Liu, S.C., 1988. On the nonlinearity of tropospheric ozone. *Journal of Geophysical Research* 93, 15879–15888.
- Liu, S.C., Trainer, M., Fehsenfeld, F.C., Parrish, D.D., Williams, E.J., Fahey, D.W., Hubler, G., Murphy, P.C., 1987. Ozone production in rural troposphere and implications for regional and global ozone distributions. *Journal of Geophysical Research* 92, 4197–4207.
- McKeen, S.A., Hsie, E.Y., Liu, S.C., 1991. A study of the dependence of rural ozone on ozone precursors in the

- eastern United States. *Journal of Geophysical Research* 96, 15377–15394.
- Milford, J.B., Gao, D., Sillman, S., Blosser, P., Russell, A.G., 1994. Total reactive nitrogen (NO_y) as an indicator of the sensitivity of O_3 to reductions in hydrocarbons and NO_x emissions. *Journal of Geophysical Research* 99, 3533–3542.
- Nowaki, P.P., Samson, J., Sillman, S., 1996. Sensitivity of urban airshed model (UAM-IV) calculated air pollutant concentrations to the vertical diffusion parameterization during convective meteorological situations. *Journal of Applied Meteorology* 35, 1790–1803.
- NRC, 1991. *Rethinking the Ozone Problem in Urban and Regional Air Pollution*. National Academy Press, Washington, DC, 524pp.
- NRC, 1999. *Ozone-Forming Potential of Reformulated Gasoline*. National Academy Press, Washington, DC, 212pp.
- Odman, M.T., Ingram, C.L., 1996. Multiscale Air Quality Simulation Platform (MAQSIP): source code documentation and validation. Technical Report ENV-96TR002-v1.0, MCNC, Research Triangle Park, NC 27709, 83pp.
- Olszyna, K.J., Bailey, E.M., Simonaitis, R., Meagher, J.F., 1994. O_3 and NO_y relationships at a rural site. *Journal of Geophysical Research* 99, 14557–14563.
- OTAG, 1997. OTAG final report. Available online at <http://www.epa.gov/ttn/rto/otag/finalrpt>.
- Pielke, R.A., Uliasz, M., 1998. The use of meteorological models as input to regional and mesoscale air quality models: limitations and strengths. *Atmospheric Environment* 32, 1255–1466.
- Pleim, J.E., Chang, J.S., 1992. A non-local closure model for vertical mixing in the convective boundary layer. *Atmospheric Environment* 26A, 1455–1466.
- Porter, P.S., Rao, S.T., Zurbenko, I.G., Dunker, A.M., Wolff, G.T., 2001. Ozone air quality over North America: Part II—an analysis of trend detection and attribution techniques. *Journal of the Air and Waste Management Association* 51, 283–306.
- Rao, S.T., Zurbenko, I., 1994. Detecting and tracking changes in ozone air quality. *Journal of the Air and Waste Management Association* 44, 1089–1092.
- Rao, S.T., Zurbenko, I., Neagu, R., Porter, S., Ku, M., Henry, R., 1997. Space and time scales in ambient ozone data. *Bulletin of the American Meteorological Society* 78, 2153–2166.
- Roselle, S.J., Schere, K.L., 1995. Modeled response of photochemical oxidants to systematic reductions in anthropogenic volatile organic compound and NO_x emissions. *Journal of Geophysical Research* 100, 22929–22941.
- Russell, A., Dennis, R., 2000. NARSTO critical review of photochemical models and modeling. *Atmospheric Environment* 34, 3503–3509.
- SAI, 1995. User's guide to the variable-grid Urban Airshed Model (UAM-V) SYSAPP-95/027, 128pp.
- Seinfeld, J.H., 1986. *Atmospheric Chemistry and Physics of Air Pollution*. Wiley-Interscience Publication, New York.
- 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. *Journal of Geophysical Research* 100, 14175–14188.
- Sillman, S., Samson, P.J., 1995. Impact of temperature on oxidant formation in urban, polluted, rural and remote environments. *Journal of Geophysical Research* 100, 11497–11508.
- Sistla, G., Hao, W., Ku, J.Y., Kallos, G., Zhang, K., Mao, H., Rao, S.T., 2001. An operational evaluation of two regional-scale ozone air quality modeling systems over the eastern United States. *Bulletin of the American Meteorological Society* 82, 945–964.
- SMRAQ, 1997. The SMRAQ project: development and application of a seasonal model for regional air quality. Available online at <http://enviro.ncsc.org/SMRAQ>.
- Tesche, T.W., McNally, D.E., Wilkinson, J.G., Loomis, C.F., Emigh, R.A., 1996. Initial estimates of emissions reductions needed for ozone attainment in Pittsburgh-Beaver Valley ozone nonattainment area. Report Prepared for: south-western Pennsylvania Clean Air Stakeholder Group, Alpine Geophysics, LLC, Covington, KY.
- US Environmental Protection Agency, 1991. Guideline for regulatory application of the Urban Airshed Model. EPA-450/4-91-013.
- Wheeler, N., et al., 1998. Development and implementation of a seasonal model for regional air quality. Proceedings of the Air and Waste Management Association's 1998 Annual Meeting. Paper 98-A739, A&WMA, Pittsburgh, PA.
- Zurbenko, I.G., 1986. *The Spectral Analysis of Time Series*, North-Holland, Amsterdam, 241pp.
- Zurbenko, I.G., 1991. Spectral analysis of nonstationary time series. *International Statistical Review* 59, 163–173.