MODEL REPRESENTATION OF LOCAL "AIR QUALITY CLIMATOLOGY"

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1. INTRODUCTION

Computer models of air quality are used extensively for environmental planning and determining compliance with air quality regulations. Model performance is typically evaluated against observations. The observations usually represent hourly or slightly longer periods, as in the case of gaseous pollutants such as ozone, or daily periods as is typically the case for fine particle ($PM_{2.5}$) levels. In all cases, model performance is measured by comparing simulated and observed pollutant concentrations or surface fluxes. However, a fundamental issue that is almost never examined is how well a model represents the combined characteristics of the local atmosphere. Another way of looking at it is to ask "How well does a model represent the overall air quality climatology of a given location?" Tables of individual model performance statistics for 8-hour average ozone mixing ratios or 24-hour average $PM_{2.5}$ concentrations do not provide information on how well a model replicates the mix of pollutants and meteorological conditions that determine local pollutant exposures at a monitoring site or of a population group.

This paper examines in a preliminary manner the concept of air quality climatology and the ability of a model to simulate the local mix of conditions that are observed. To do this requires that the definition of "climatology" be stretched to include periods shorter than those usually considered in a formal climatological analysis. A climatologist would take issue with calling any study period less than a decade (or even several decades) a climatological study because defining climate usually requires observations on a multi-decadal time scale. Another factor hindering an analysis of air quality climatology is the lack of observations. With few exceptions, most air quality data bases are too short to represent climatological averages. Finally, laws and regulations have been successful in improving local air quality, but this implies changes in conditions that are on a time scale shorter than 10 years. Nevertheless, it is useful to think about air quality in terms of its "climatology" at different locations because of what such terminology implies regarding the identification and recurrence of recognizable patterns of weather and pollutant mixtures. Hence, for the remainder of this paper the term "climate" and its derivatives will be used very loosely, recognizing that existing data are generally insufficient to truly define local air quality climate in the strictest sense of the word.

The next section describes the models used to simulate local air quality and the data used to evaluate the simulations. Section 3 describes the various measures of air quality climate that were examined for this study. The results of this study are summarized in section 4 with a section on conclusions at the end.

2. ANALYSIS METHODOLOGY

2.1. Models

This study relied on two models that are used extensively for air quality analysis. Meteorological conditions were simulated using the MM5 model (Grell *et al.*, 1995). Atmospheric chemistry was simulated using version 4.6 of the CMAQ photochemical and aerosol model (US EPA, 1999). CMAQ was configured with the carbon bond-IV chemical mechanism. Inorganic aerosol growth in the presence of gas-phase constituents was simulated by CMAQ using the ISORROPIA model (Nenes *et al.*, 1998). Emissions inputs to CMAQ were prepared using the Models-3/SMOKE version 2.2 emissions processing system [US Environmental Protection Agency (USEPA) documentation: http://www.smoke-model.org/version2.2/manual.pdf]. Reported hourly emissions data from large point sources for May-August 2003 were

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acquired from a USEPA web site (http://cfpub.epa.gov/gdm). Emissions for smaller point sources and area sources were assumed to be the same as those processed for 2002 by the VISTAS Regional Planning Organization (http://vistas-sesarm.org). This approach introduces some error into model results because of a less than perfect match between emissions of certain sporadic sources (such as wild fires) and observed concentrations. Such error most likely affected results for elemental carbon and organic aerosols. The resulting uncertainty could not be avoided without undertaking a huge effort to develop day-specific emissions, an effort that was well beyond the scope of this project.

Modeling was done using a computational grid composed of 36-km (square) grid cells. This was the same grid used by VISTAS for its regional haze modeling and was selected for compatibility with VISTAS emissions and so that results would be applicable to the general level of spatial resolution being used for regional haze. Note that modeling for $PM_{2.5}$ attainment demonstrations is likely to be performed at higher spatial resolution using grid cells of 12 km or smaller. The preliminary nature of this investigation was such that high resolution modeling was not justified at his time. However, the methods used here would be equally applicable to modeling done at higher resolution.

2.2. Observations

Data availability and the general characteristics of observed pollutants determined the time period examined for this study. The original motivation for this work was to focus on the ability of the CMAQ to replicate the large variability observed in aerosols that influence atmospheric visibility. Thus, the available aerosol data were of primary importance in selecting the period examined.

Continuous (hourly) data on $PM_{2.5}$ and its constituents were available from the Great Smoky Mountains (GSM) research station located at the western end of the Great Smoky Mountains National Park in east Tennessee at a site called Look Rock. Look Rock monitoring was supported by the VISTAS Regional Planning Organization (http://vistas-sesarm.org) and began in spring of 2003. Other data that used in this study included 24-hour speciated $PM_{2.5}$ concentration data from the IMPROVE network (Malm *et al.*, 1994), daily and continuous speciated $PM_{2.5}$ concentration data from the SEARCH network (Hansen *et al.*, 2003; Edgerton *et al.*, 2006), and continuous aerosol data reported on the EPA AIRS Air Quality Subsystem (AIRS/AQS) (http://www.epa.gov/ttn/airs/airsaqs/index.htm). Due to the widespread availability of hourly ozone data, the importance of photochemistry in secondary aerosol formation, and the importance of ozone as a co-pollutant in an area's air quality climate, ozone data were added to the data base used to evaluate modeled air quality climatology. Data from numerous monitoring stations are available for 2003 but of greatest interest were those stations that included data on continuous speciated and total $PM_{2.5}$ mass concentrations, ozone and wind measurements. This consideration eliminated many from the mix of monitoring stations included in the analysis.

An examination of time series plots of hourly ozone, sulfate and total $PM_{2.5}$ from Look Rock (Figure 1) indicated that the period of May-August 2003 was interesting because of the occurrence of interspersed periods of clean and polluted air masses. Again, it is not possible to characterize air quality climatology at a given location with only three months of data. This analysis is seen as an effort to introduce the concept of "air quality climatology." Perhaps this work can motivate the air pollution community to think about what AQC means, how it can be described, and how to test air models for their ability to replicate important features of AQC. Groups such as VISTAS are already relying on models to guide them on how to best identify sources that significantly impact visibility (regional haze) at a target site. Wind roses and associated air pollutant concentrations come into play in these analyses of "areas of influence" as States examine ways to get additional visibility improvements beyond those already expected from current regulatory actions. Thus, the concept of air quality climatology is a meaningful concept in the air regulatory arena.

3. DESCRIBING LOCAL AIR QUALITY CONDITIONS

3.1. Airflow

Local airflow plays an important role in determining which sources have critical impacts during high atmospheric pollutant loadings.

Even in the case of regional haze in Class 1 areas, winds determine the extent to which nearby sources influence local visibility, making them targets for additional emission controls. Models are used to predict the benefits of those controls. However, models that cannot replicate local conditions contributing to haze or other air quality effects of concern become at best useless tools and, at worst, hindrances to achieving desirable air quality management objectives. The ability of a model to simulate local airflow patterns is of great importance in understanding how well the model may simulate impacts of local emissions and the expected benefits of controls on nearby sources. Coupling data on the distribution of local wind direction with the typical air quality associated with each direction is one way to examine a model's potential usefulness for simulating important source-receptor relationships.

Ozone and aerosol data were matched with wind observations to create the beginnings of an air quality climatology for each site. Winds were measured at most monitoring sites studied here. In those few cases where it was not measured at the site, data from the nearest National Weather Service station were used. The only sites to use NWS wind data were one in Chicago (CCI) and one in Charlotte (CLT).

3.2. Pollutants

The most useful data for describing local air quality climatology are hourly gaseous pollutant and aerosol concentrations. Unfortunately, hourly aerosol data were just beginning to be collected in 2003. This leaves most sites with only 24-hour aerosol concentrations. Of those sites, most only collect total $PM_{2.5}$ mass and do not routinely measure aerosol chemical composition. Even sites that collect 24-hour total $PM_{2.5}$ mass do not operate continuously but instead collect data intermittently with measurements usually made only every third day. This greatly limits the potential for characterizing local air quality climatology. Thus, in many locations, the only way to obtain air quality climate information is to model conditions for an extended period of time. But can models provide accurate information? This study tries to address that question.

Table 1 lists the sites used in this analysis. Not all sites measured all targeted pollutant species. Some other sites reported data but the quantity of data was very limited during the period of study. Many more ozone monitoring sites exist but were not included so as to keep the number of sites investigated manageable.

4. RESULTS

4.1. Wind Characteristics

The number of observations of air pollutant species during the May-August 2003 simulation period was not large enough to support an analysis that used the traditional 16 wind direction sectors. Instead, winds were sorted into 8 45° direction sectors (north, northeast, east, etc.) This allowed computation of more robust sector-specific statistics for winds as well as pollutant species. A comparison of hourly model and observed wind sector frequencies for each site revealed that modeled frequencies more closely resembled observed values for higher wind speeds. The model performed poorly for winds <2 m s^{-1} with little if any correlation found. For winds >2 m s^{-1}, the model sector frequencies across all sites agreed with those observed a significant fraction of the time with a linear least-squares regression r^2 = 0.39. More importantly, when a regression was done forcing the fit through the origin the slope was 0.86 indicating little bias in the frequencies, and implying model skill in identifying the most and least frequent wind direction sectors. However, the model performed better at some sites (Figure 2, left side) than others (Figure 2, right side). Most cases of poor performance are like site PNS—the model typically is off (rotated) one sector in its representation of the wind direction maximum and minimum sectors.

The model struggled with wind speed, simulating totally unrealistic diurnal speed patterns consistent with what has been found elsewhere (Zhang and Zheng, 2004) This is an apparent weakness in the boundary layer turbulence parameterization that incorrectly simulates vertical momentum transport under convective conditions. However, examining the mean speed by direction revealed that the model tended to identify those directions most prone to lower and higher than average wind speed. Figure 3 illustrates sites at the extreme of model performance. The model did an excellent job of replicating the direction-driven wind speed behavior at sites like OAK and YRK while greatly missing the mark at GSM and CLT. For both wind speed and direction, a model's

ability to capture the near-surface wind characteristics of a site is most dependent on its ability to identify local surface physical features that strongly influence airflow. A model is more likely to have problems doing this in complex terrain (e.g., GSM) and urban environments (e.g., BHM, CCI, CLT and JST).

4.2. Ozone

An examination of ozone results is in order because ozone modeling is more mature than that for aerosols and is somewhat less complex. In addition, it could be useful to contrast different model behaviors for ozone versus fine particles. The CMAQ simulation done for this effort consistently underestimated ozone levels at each site. This is likely due in large part to the relatively low spatial resolution of the grid. However, comparative details between sites and between pollutant species are more important for this analysis than are actual values. The CMAQ ozone bias means that model results for ozone exposures (e.g., to specific local populations) underestimate local conditions. Table 2 summarizes the local ozone exposures at each site for the most exposed direction sectors. Ozone exposure index (OEI) is represented by the sum of all hourly ozone mixing ratios that exceed 0.06 ppm during the modeled period, expressed as ppm-hours. This index is often used to represent the exposure of sensitive vegetation to ozone levels but is used here as a surrogate for the ozone exposure of people who live near each monitoring site.

All ozone metrics indicate that CMAQ generally underestimated ozone at each site. The time-integrated OEI is much greater when computed from observed values than from model values, and the model rarely identified a direction sector for highest ozone exposure that matched with sectors identified from observations. The highest observed one-hour ozone values were always substantially greater (average difference 40 percent) than those modeled. Even the average daytime peak ozone levels were typically higher than modeled. There is no doubt that the model did not produce sufficient amounts of ozone in both the rural and urban areas. This bias may have been caused by insufficient model emissions of ozone precursors—especially NO_x, it may have been due to modeled meteorology producing conditions that were biased against the formation of higher ozone in the boundary layer, or at some sites it may simply be a matter of low model spatial resolution. This issue was also a problem for VISTAS during its modeling of regional haze (T. Tesche, personal communication) but was not examined in great detail nor was it considered a sufficient reason for concern because VISTAS focus is on fine particle formation, not ozone.

4.3. Fine Particles

Daily $PM_{2.5}$ and components

Most particulate data are 24-hour averages of aerosol mass concentrations. Only a handful of sites measured continuous (i.e., hourly) aerosol mass during this period. Of the daily sampling sites, most collected samples on an intermittent schedule—once every third day for SEARCH and IMPROVE network sites. Figure 4 summarizes the distributions across all sites examined here of 24-h concentrations of total $PM_{2.5}$ mass along with sulfate, organic and elemental carbon fine particles. One common feature of all distributions is the relative lack of observed data that fall into the lowest concentration bin. The reason for this is that the model provides a continuum of values for each particle species but observations are limited to cases when the mass collected on filters is greater than the minimum detectable limit for the analytical method used. For model results, the lowest bin is not the most populous but is often in the 2 to 4 most populated bins. Thus, model results have a built in bias for averaging less than observations simply because the latter cannot detect concentrations when ambient levels are very low.

Given this bias, a fair way to compare the two sets of distributions is to determine whether the most populated concentration bin representing model values is within one category of the most populous observation bin. The model and observed most populous bins are the same for both sulfate and total $PM_{2.5}$. For elemental carbon particles the most populous model bin is one category below that observed. The largest discrepancy is for organic aerosols where the most populated model bin is two categories below that observed. Overall, average model concentrations (Table 3) averaged 22 percent high for sulfate, 26 percent low for organic aerosols, 58 percent low for elemental carbon, and only 3 percent high for $PM_{2.5}$. High biases in sulfate tended to be offset

by low biases in other species. CMAQ simulated only about half the levels of ammonium that were measured. This bias—coupled with the overestimate of sulfate—contributed to the extreme underestimates of nitrate. The result for $PM_{2.5}$ is an example of getting good model performance that masks inherent problems for individual components of the fine particle mass system. Nitrate aerosol is ignored for the remainder of this paper due to the total lack of model skill in simulating it for the 2003 spring-summer period.

Local exposures to aerosols—and the ability of the model to accurately link sources with those exposures—can be examined by comparing site by site average aerosol concentrations by wind direction (Figure 5). The model clearly has skill in reproducing the spatial patterns associated with sulfate and organic aerosols. This alone is sufficient to provide skill in simulating patterns of $PM_{2.5}$. Also, except for one site (BHM), the model had some skill in replicating the range in elemental carbon.

Two characteristics examined when comparing the site-specific model and observed climatology of $PM_{2.5}$ and its components were how well the model represented the observed directional variability of each fine particle species and how well the model reproduced the extremes in each species. Model-derived directional distributions of 24-h $PM_{2.5}$ and its components required the calculation of a daily mean direction. Wind speed was ignored (given the large model errors in assigning speed by hour) so that the mean daily direction was derived by simply averaging the east-west and north-south component vectors for unit wind speed across all hours of a day. Some wind directions had few or even no observations. Unless explicitly stated, the following discussion compares model and observed conditions only for those direction sectors with significant amounts of data.

Daily observed and modeled mean aerosol concentrations (except nitrate) as a function of 24-h wind direction are plotted in Figure 6 for the urban site BHM. Directions with no data are left blank in the radar plots. At site BHM, the north wind direction had the highest mean observed sulfate concentration while the southeast direction had the lowest value. CMAQ produced the highest sulfate for the northwest direction, but it only had one day in the data set. The highest mean model value for a sector with multiple days was north, matching the direction sector with that same distinction in the observed data set. The lowest mean sulfate corresponded with the northeast sector in the model. The directional signal for organic aerosols was quite different. Observations indicated that the northeast sector produced the highest organic aerosol concentrations with the lowest associated with airflow from the south. The model produced the highest organic aerosols when the wind blew from the west and the lowest occurred with winds blowing from the south. In this case, the lowest concentrations in both the model and observed data coincided with the same direction of origin but the highest values did not.

The ammonium directional pattern matches closely with the sulfate pattern in the observed data base. This is not entirely true in the model which produced the highest ammonium levels with airflow from the north and northwest sectors, but the latter was—as with sulfate—based on only one day. The lowest model ammonium coincided with a south wind whereas the southeast had the lowest in the observations. Given the difficulty of trying to model near-surface airflow, a directional difference of one sector in this comparison is probably not very significant.

The story for elemental carbon (EC) is quite different from that of sulfate and ammonium. The model grossly underestimated EC and showed little concentration variation with direction. Observations show a strong maximum for northeast airflow that corresponds with the maximum in organic aerosol levels. Analytical difficulty in clearly delineating observed OC from EC implies that the similarity in the maximum directions for these particle species may not be coincidental.

Finally, $PM_{2.5}$ shows a pattern that is a blend of patterns of the most dominant particle species. Highest observed $PM_{2.5}$ comes from the northeast. Highest modeled $PM_{2.5}$ comes from the north (no fewer than 5 days were associated with any direction sector for $PM_{2.5}$, modeled or observed). The lowest observed $PM_{2.5}$ came from the south; the lowest modeled $PM_{2.5}$ came from the southwest. As mentioned previously, a difference of one direction sector is not significant.

It is impractical to show plotted results for each of the other sites. Instead, Table 4 contains a summary for each site of the highest and lowest aerosol concentrations when averaged by direction sector. These results indicate the model performed best at identifying sulfate, ammonium and $PM_{2.5}$ mass peaks while it did poorly identifying organic and EC aerosol mass peaks. However, for direction minima the model did slightly better for organic aerosol than even sulfate, and overall identified $PM_{2.5}$ minimum directions better than for any individual species. One interpretation of this result is that first, the spatial emissions distribution is known better for sulfate than any of the other species. Thus, the model shows skill in finding the direction maximum for sulfate (and its usually related ammonium component). On the other hand, lowest $PM_{2.5}$ levels may be more likely associated with meteorological rather than emissions factors, especially precipitation. Precipitation is usually more often associated with a southerly wind component than any other direction (especially in the southeastern United States) and most observed and modeled $PM_{2.5}$ minima show that kind of association.

As for site-specific performance, the model exhibited large variations in ability to capture aerosol maxima and minima by direction. Sites CTR and OAK were both well characterized with all maximum and minimum concentration directions being identified within one direction sector. In contrast conditions at sites GSM (only two sector matches), YRK (3 sector matches) and OLF (4 sector matches) were not well represented. Of all the sites, GSM is in the most complex terrain and this may be the primary factor influencing poor model performance. Local topographically-induced air circulations must be accurately portrayed by the model for it to realistically replicate variations in pollutant concentrations. The relatively coarse spatial resolution of the 36-km grid means that simulated airflow at GSM is unlikely to reflect local terrain influences.

Model difficulties replicating conditions at YRK and OLF are not as easily explained. Both sites are located outside urban areas (YRK is occasionally influenced by Atlanta and OLF is similarly influenced by Pensacola). Simulated wind directions were not especially accurate at YRK but they were done well at OLF. The close proximity of major urban and other industrial sources makes the accurate simulation of wind direction especially critical at these near-urban locations for reproducing pollutant variability by direction. Direction errors may be an important factor in poor model performance at YRK but they do not appear to be an issue for OLF. However, at OLF there appears to be only a small difference between the airflow from the cleanest sectors (south through southwest) and the most polluted (west through northwest). Low model spatial resolution and the nearby influence of airflow off the Gulf of Mexico may be the factors that most challenge the model at OLF and contribute to its poor performance.

The best overall model performance for identifying pollutant variability by direction was found at the CTR and OAK sites. The model did not have superior performance in identifying airflow patterns at these sites—especially when compared to the other locations—but it did have a good balance between simulating reasonable airflow patterns and aerosol concentration variability by direction. This suggests that there is a fine line separating high quality model performance versus medium and low quality performance in this regard.

Hourly $PM_{2.5}$ and components

There is a potentially large difference between a model's ability to simulate daily (24-h) and hourly aerosol concentrations. Factors influencing this difference include the temporal and spatial accuracy of emission rates, the spatial resolution of the model grid, the simulated occurrence of meteorological conditions affecting secondary aerosol formation, and the local complexity of terrain and land cover features that influence aerosol transport and dispersion near a site. The ability to measure continuous (pseudo-hourly) speciated aerosol concentrations involves the deployment of newly developed technology. This technology is still being tested and refined and few data bases of this type exist, especially during the period that was simulated.

A few sites were found the have continuous aerosol data of some type. Most sites that do exist had only continuous $PM_{2.5}$ mass (mostly from so-called TEOM devices, Chuersuwan *et al.*, 2000). These instruments measure the build-up of aerosol mass on a micro balance and suffer from some measurement biases (**ref.**), but do a reasonably good job of identifying short-term variations in fine particle mass as long as

certain precautions are taken. These precautions were taken in collecting the $PM_{2.5}$ data used here. Other instrumentation is now being deployed to measure speciated aerosols—especially sulfate, nitrate, organic and elemental carbon mass. A suite of these instruments were deployed at the GSM site during the simulation period as well at some SEARCH sites. Similar measurements are now being made at other sites but the data of record begins after August 2003. Thus, the analysis reported here represents only a preliminary examination of high time resolution modeled aerosol results compared against measurements.

Site GSM

At GSM, modeled hourly concentrations reflected the same biases found for the modeled 24-h concentrations when compared against daily observed aerosol levels. The sample size ranged from 1600 for OC to over 2500 for $PM_{2.5}$. This compares to the smaller daily concentration sample size of 30 or so observations for sulfate, other $PM_{2.5}$ components and total $PM_{2.5}$ mass. Hourly wind direction variations respond quickly to changes in local meteorological conditions and may do a better job of associating aerosol concentrations with local airflow conditions, especially at a complex site like GSM. Figure 7 illustrates the directional variations in mean hourly aerosol concentrations at GSM. Direction-specific concentrations have been normalized by the overall average concentration for each species to remove the effect of model biases. This simplifies a comparison between the two sets of concentrations to facilitate focusing on aerosol directional variations, especially directions associated with the lowest and highest average values. Sulfate peaks occurred with GSM winds blowing from the northwest and north, while modeling indicated peaks occurred with airflow from the north and northeast. For OC, the highest observed levels were associated with northwest winds with the model indicating southwest winds. The daily concentration wind roses provided similar results for sulfate but not OC (Figure 7) for which winds from the south had the highest observed concentrations. One common feature for hourly sulfate, OC, EC and $PM_{2.5}$ was the apparent clockwise rotation of modeled peak concentration directions compared to observed peak directions. This result is probably caused by the local influence of the ridge on which the GSM site resides. The ridge appears to cause persistent northwest (locally perpendicular, upslope) airflow. The model—using low resolution—cannot resolve the ridge and rotates the winds to align with the smoothed southwest-to-northeast oriented axis of the southern Appalachian Mountains. Nitrate has a completely different story. As it did for 24-h nitrate, the model did a poor job of simulating hourly nitrate—in part because nitrate levels are closely tied to the availability of free ammonia. From the 24-h data it is known that the model underestimated particulate ammonium (and hence, ammonia), but determined that a nitrate spike in hourly data existed with easterly airflow. Nothing of the sort was found in the observations, leading to the conclusion that the model identified a source of ammonia east of GSM that was able to impact local nitrate levels in spite of the usual abundance of sulfate.

The value of having hourly aerosol data for evaluating model performance is illustrated by the previous discussion. The short-term concentrations provide a clearer picture of both model and actual aerosol behavior than is obtained from analyzing 24-h data. This is critically important when examining air quality in complex terrain or in a complex urban setting with many nearby primary and secondary aerosol pollutant sources. The greater temporal coverage of the continuous sampling also provides a better representation of model behavior than can be achieved when looking at data collected only every third day as was the case for the 24-h concentrations.

An additional result that was not found in the daily aerosol data was the unexpected variation in model skill at the hourly level associated with the different aerosol species. A simple linear regression of each model versus observed species concentration revealed that the highest degree of association (r^2=0.30) occurred for organic aerosols (OC). Conventional wisdom has been that aerosol models have the most skill simulating sulfate. However, the version of CMAQ used for this study included updates to the secondary organic aerosol treatments as outlined by Morris *et al*. (2006). When these treatment updates were included, the prevalent CMAQ low bias for OC was largely removed. Surprisingly, EC was the second most skillfully simulated aerosol species (r^2=0.24) followed by sulfate (r^2=0.21). For $PM_{2.5}$, model skill (r^2=0.28) followed closely with that for OC. No skill

existed for nitrate. The reason why CMAQ performed better for OC than sulfate at GSM is unknown. Both aerosol species are sensitive to precursor emissions and meteorological factors. The most obvious difference is that sulfate is primarily the secondary product of anthropogenic emissions that are not uniformly distributed and experience temporal emissions variability distinctly different from that of the organic gaseous precursors for OC. A large fraction of the OC precursors are natural in origin (Seinfeld and Pandis, 1998) and their emissions tend to be more uniformly distributed. Thus, errors in airflow direction alone may account for less model skill in simulating sulfate than OC, independent of the other meteorological factors that also must influence secondary aerosol formation.

One ratio of interest is the fraction of total aerosol carbon that occurs as EC, $R_{EC/TC}$ (TC=EC+OC). The wind rose distribution of mean $R_{EC/TC}$ (Figure 8) shows that the observed values were greater than modeled values for all directions. This bias could be related to poor knowledge of EC emissions, which are notoriously difficult to model as their greatest source is open burning, including wildfires. The EC bias may also be due in part by the analytical method used because EC is defined by the assumptions made to quantitatively measure it. That said, the bias in $R_{EC/TC}$ might be overlooked except that at GSM the observed bulge is much greater for airflow from the northwest clockwise through southeast whereas the modeled maximum is associated with airflow from the west clockwise through northeast sectors (again, the industrialized, populated Tennessee Valley.

Other ratios of interest include sulfate-to-$PM_{2.5}$ ($R_{SO4/PM}$) and TC-to-$PM_{2.5}$ ($R_{TC/PM}$). Again, Figure 8 illustrates the variability of those ratios by wind direction for site GSM. CMAQ overestimated $R_{SO4/PM}$ for southwest clockwise through northeast sectors and underestimated $R_{SO4/PM}$ for east and southeast sectors, with modeled peak sectors rotated counterclockwise. CMAQ overestimated $R_{TC/PM}$ for northeast clockwise through southeast sectors but replicated the ratio very well for the other sectors. Again, the modeled maximum in $R_{TC/PM}$ (east and southeast) was rotated counterclockwise from that observed (south). These examples indicate a consistent rotational bias in model results that is probably associated with airflow simulation issues, a likely model bias in EC emissions, and model biases in SO_2 and OC (or its precursor) emissions and/or sulfate and secondary OC aerosol formation rates for certain directions. Given the relatively few 24-h aerosol observations and the variability of wind direction from one hour to the next, most of the model behavior just described is unlikely to be discerned without examining hourly aerosol measurements.

Site CCI

An urban site that reported continuous sulfate measurements without other hourly data was monitoring station "CCI" in Cook County (Chicago) Illinois. Figure 9 is the normalized sulfate aerosol wind rose for CCI. When compared with the equivalent sulfate plot for GSM in Figure 7 it is evident that the model rotated both sulfate concentration maxima about one direction sector from the observed maxima. The rotation was clockwise at GSM but counterclockwise at CCI. Whereas local terrain influences may have controlled model biases at GSM, the rotation at CCI was more likely due to the fact that winds representing CCI were not measured at the site and were instead used from the nearest National Weather Service station at Chicago O'Hare airport. Subtle differences in local surface features (buildings, hills, and so forth) can be sufficient to create disparities in airflow characteristics at nearby sites. Despite the directional bias at CCI, model skill in replicating hourly sulfate levels was actually considerably higher there (r^2=0.37) than at GSM.

SEARCH Sites

Continuous $PM_{2.5}$ and speciated mass data were collected at four SEARCH sites: BHM, CTR, JST and YRK. Table 5 lists the fraction of total variance (r^2) that was found to be shared by both the modeled and observed hourly aerosol concentrations for the SEARCH sites, CCI and GSM. This measure of model skill varied widely across sites and species. For these sites, CMAQ generally performed best for OC and sulfate, and poorest for nitrate and EC. CMAQ actually performed slightly better for total carbon (TC) than sulfate or OC alone. Model skill for total $PM_{2.5}$ mass was better than for individual components at both urban sites and one non-urban site (GSM). Perhaps the biggest surprise was the total inability of CMAQ to show skill in

simulating sulfate aerosol for site BHM (Birmingham, Alabama). The best explanation for this is that the sulfur emissions characterization for sources surrounding Birmingham was of especially low quality compared to that for sources impacting the other sites. Also, the unexpectedly high level of skill suggested for nitrate at BHM is probably a statistical anomaly given the large mismatch between mean observed (0.5 μg m^{-3}) and computed (0.01 μg m^{-3}) concentrations.

Joint Spatial-Temporal Aerosol Patterns

The hourly SEARCH data, together with the hourly GSM data and the continuous sulfate data from CCI, offer a unique opportunity to examine in-depth model treatment of aerosols. From the perspective of understanding local "air quality climatology" it is important for a model to be able to accurately portray the spatial and temporal relationships that most influence pollutant levels at a site. These relationships are not clearly defined when only daily average concentrations are available. A useful diagram for comparing observed and modeled spatial-temporal air quality variations is one that combines both dimensions along its two axes. Figure 10 illustrates the concept for ozone at site BHM. These plots may be prepared using all data plotted separately as unique points with contours applied to the resulting two-dimensional ozone field. However, the result is very messy and has limited usefulness. Also, limited quantities of data for some portions of the space-time (S-T) plot result in holes that must be "filled" by either a human or an automated imputation algorithm. This problem was minimized by first assigning ozone values to various sections or blocks of the S-T plot and then averaging all the values within a block. For all plots shown here, the averaging sections were defined by dividing each day into 6 equal 4-hour blocks of time centered on midnight, 0400, 0800, noon, 1600 and 2000 local time. Likewise, wind direction (the surrogate for spatial pollutant distributions) was divided into 6 equal 60-degree blocks of wind direction centered on 0°/360°, 60°, 120°, 180°, 240° and 300°. This created 36 spatial-temporal blocks of data per plot. Contours of block-averaged ozone mixing ratios were then computed using the block averages plotted at the appropriate coordinates of each diagram. This method results in spatial and temporal smoothing that eliminates much of the data noise while retaining the most dominant features in the data field. All subsequent S-T plots were created using this approach.

The observed ozone S-T plot in Figure 10 indicates that ozone tends to reach a maximum value between noon and 1600 local time regardless of wind direction. Highest ozone levels are associated with local airflow blowing from between 30° and 90° (i.e., centered near 60°) with a secondary maximum (not shown due to limited contour resolution) occurring for winds blowing from between 300° and 360°. A local ozone minimum occurs within the afternoon ozone peaks when winds blow from the south (180°). This minimum could be associated with higher density NO emissions to the south, which result in local ozone titration, or with a greater frequency of afternoon cloud cover with southerly winds. In either case, a skillful model should be capable of reproducing these major features of BHM's ozone S-T behavior. In the S-T plot for simulated ozone fields (Figure 10), the primary features are (1) the model does not produce values as high as the maximum observed ozone levels nor as low as the minimum observed ozone levels (this is likely due in large part to the relatively low spatial resolution associated with using 36-km grid cells); (2) the model does capture the afternoon ozone maximum with good timing, and (3) the model is only slightly off in its reproduction of the local minimum—centered near 140° rather than 180°—embedded in the afternoon ozone maximum.

CMAQ performance for ozone varied across the different sites and was generally better for urban than non-urban sites. Model performance at BHM was the best of all the sites. Thus, results in Figure 10 serve as the template for what would be nearly ideal model behavior for aerosols. S-T plots in Figure 11 compare model results and observations for sulfate aerosol at all six sites for which hourly data were available. The primary differences between these comparisons and those done to produce the values in Table 5 are that these represent averages over blocks of several hours of data (Table 5 represents a direct one-to-one comparison of hourly values) and the data in Figure 11 are based separately on observed and modeled wind directions. A direct comparison of hourly values often mixes observed and modeled directions that do not match because the model does not always agree with observed

airflow. Thus, Figure 11 S-T plots allow a comparison between observed and modeled S-T relationships that is "direction-aligned."

Notable findings are summarized here by site:
BHM – CMAQ captured the observed afternoon peak in sulfate but overestimated its magnitude. Observed nighttime sulfate minima align with southerly airflow whereas CMAQ produced a morning minimum aligned with 120° airflow and a midnight minimum aligned with 300° airflow. The CMAQ minimum at 1600 local time and 60° airflow has an observed counterpart shifted 4 hours later.
CTR – CMAQ captured the broad low in observed sulfate for winds blowing from 120°-240°. The observed overnight sulfate maximum for 300° winds was not well represented by the model which instead shows a late afternoon maximum centered on northerly (360°) winds.
CCI – CMAQ produced a local sulfate maximum for winds blowing from between 60° and 180°. This maximum was an overnight phenomenon in the model, but occurred in late afternoon in the observed values and for winds centered on 180°. The local sulfate minimum was observed at 0400 local time for winds from 300° but was simulated 1200-1600 local time with winds from 360°.
JST – Observed sulfate was greatest in late afternoon, especially with winds blowing from 120° clockwise through 300°. CMAQ greatly overestimated sulfate concentrations. It produced a broad peak (between 1000 and 1800 local time) that occurred for most directions but was especially high centered on 180° (contour details not shown). Local sulfate minima were observed in early morning (180°-240°) and near midnight (360°) but CMAQ placed a local minimum between midnight and 0400 for 0°-60° winds.
YRK – The CMAQ S-T sulfate field looks very much like that for JST. The modeled sulfate peak occurred near 1600 local time and was found for winds blowing from north clockwise through south. This matched the observed timing and airflow orientation fairly well. The observed local minimum was much broader than modeled, occurred later in the morning and with a different airflow orientation.
GSM – CMAQ produced a local sulfate maximum centered near noon for winds from between 60° and 120°. The observed sulfate minimum actually occurred at this location in the S-T plot. The CMAQ minimum occurred with the same wind direction but later in the afternoon. In general, observed sulfate was higher with winds from between 300° and 60° and the model replicated these higher levels for the most part. This was the only site characterized by complex terrain and modeling airflow and the timing of pollutants arriving from elsewhere is particularly challenging for this type of environment.

Both observed and modeled S-T distributions of carbonaceous aerosol showed less variation than for sulfate, especially in non-urban environments. The urban sites had the most inhomogeneous S-T fields (Figure 12). At BHM, observed TC levels were highest with airflow from 300° clockwise through 60° during the overnight hours. CMAQ closely matched the observations in producing the highest TC levels overnight, but had a narrow window of airflow—centered near 120°—when the peaks occurred. A secondary peak for winds blowing from around 240° was also simulated. Hence, the directional alignments for the observed and simulated peaks do not overlap. At JST the observed TC S-T field was fairly smooth with slight maxima in three locations. CMAQ simulated higher maximum TC levels for the 1800 through midnight period and for all wind directions. The lowest TC levels were modeled for the midday hours. The greater variability in BHM TC levels was driven by variations in EC, with OC being fairly constant. CMAQ did not capture this variability and kept OC/TC ratios >0.9 throughout the S-T field. Both observed and simulated OC/TC ratios were fairly constant at JST and the TC S-T field lacked much variation as a result. Thus, emissions of EC (primarily of combustion origin) made the BHM TC field difficult to replicate, whereas modeled OC variability, with secondary aerosol formation playing a big part in its behavior, accounted for most of the difference between observed and modeled TC S-T fields at JST.

Aerosol nitrate and ammonium were not well handled by CMAQ and there is little value in dwelling on the modeled S-T fields. S-T plots of total $PM_{2.5}$ mass are shown in Figure 13. Although CMAQ showed some skill in replicating local aerosol maxima and minima for sulfate and carbonaceous aerosol, the composite skill for total $PM_{2.5}$ is not impressive. It appears that overall error contaminates the S-T fields to the point that very few major observed features are replicated by CMAQ. For example, at BHM the highest levels of $PM_{2.5}$ occurred between 0600 and noon when airflow was from 30° clockwise

through 210°. CMAQ instead produced a minimum in the S-T field for these conditions. Similar mismatches occurred for the other sites. These results imply that emission controls tested by the model are unlikely to be accurately reflected in model aerosol outputs. The success, as measured by lower $PM_{2.5}$ concentrations, of controlling specific sources of primary particles or particle precursor emissions cannot be known from model results. This is especially disconcerting if the goal is to target specific sources for improving visibility by a specific amount or to reduce human exposure to particulate matter for health reasons. These results also indicate that the model is not equipped to forecast particulate levels for public health advisories because, even if wind forecasts are perfect, there is little indication that the $PM_{2.5}$ forecast could have much skill.

Recent improvements in reducing model bias for specific aerosol species have done little to move models like CMAQ closer to the skill level associated with ozone. This is made clear in Table 6 which summarizes results of a least-squares comparison between observed and modeled ozone and $PM_{2.5}$ S-T fields (as defined and computed previously). At most sites CMAQ shows skill in replicating the spatial-temporal ozone patterns but no skill is evident for $PM_{2.5}$. Skill in simulating S-T patterns for sulfate and TC (Table 6)—the primary constituents of $PM_{2.5}$—are quite low and the lack of skill for $PM_{2.5}$ is not surprising. Somewhat unexpected was the difference in model skill as shown in Table 6 for S-T patterns of sulfate, TC and $PM_{2.5}$ versus the corresponding skill in reproducing these same aerosol concentrations paired hourly but not averaged by wind direction (Table 5). Averaging by direction should have eliminated one major source of uncertainty by forcing model results to align more closely with observed airflow and the pollutant transport implied for each given direction. In the case of sulfate, where source locations and emission rates are known quite accurately, this approach produced very slightly improved performance only at BHM (assuming an r^2 difference of 0.14 can be considered an improvement). Likewise, modeled TC levels only showed more skill in the direction-aligned data set for one site (CTR).

Wind direction is only one of many meteorological factors that influence pollutant concentrations. Other important factors such as cloud cover, mixing layer depth, and precipitation may have equal or greater influence on aerosol concentrations. One possible reason for the decline in CMAQ skill when results are “direction-aligned” is that the process of forcing alignment results in a mismatch in other meteorological variables. If those other variables are of equal or greater importance in determining aerosol levels then the apparent overall skill could decrease compared to what it was prior to realignment. Any meteorological factor that is tightly bound to time of day (e.g., temperature) remains mostly unmodified and is not a likely factor in the apparent skill decline because time is not realigned when the S-T plots are prepared. Ozone—which is more strongly tied to temperature than other meteorological variables—showed improvement at most sites from direction alignment, with sites BHM, CTR, JST and YRK experiencing model r^2 increases of an average 48 percent. CMAQ performance at GSM was the only site to show a decrease (from r^2 = 0.31 to 0.10). As stated earlier, this unique response is probably tied to the complex topographical situation that characterizes the site and the low spatial resolution of the simulated wind field.

5. CONCLUSIONS

A model’s ability to accurately simulate the association between local airflow and aerosol concentrations is important for identifying ways of reducing local fine particle exposures. Models like CMAQ are typically evaluated for their ability to reproduce basic statistical measures of performance such as mean, median and mean normalized concentrations, but rarely are these models subjected to more detailed investigation of their ability to link local pollutant levels to airflow characteristics such as wind direction. From the previous analysis it is evident that CMAQ—coupled with a meteorological model like MM5—is capable of limited skill in this area. However, such skill is highly dependent on location, pollutant species, and even the averaging time of the pollutant (e.g., 24-hour versus one hour).

More quantitative testing of various performance metrics beyond the standard statistical fare is needed to determine the utility of models for evaluating pollutant control strategies at a particular location. A minimum of one year of model performance is suggested due to the large variations in meteorological

conditions that affect aerosol concentrations. Also needed is some way of quantifying the abundance of non-speciated $PM_{2.5}$ in a way that enables identifying the relative importance of other species to the local $PM_{2.5}$ mix once the characteristics of the "known" species are resolved. This is important to maximize knowledge about controllable particles, especially in complex emission environments such as industrialized urban settings. The idea of a pollutant "climatology" is a useful conceptual model but it must take into account the reality of changing pollutant mixtures at local, regional and even global scales.

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Table 1. Ozone and aerosol monitoring sites that collected data used in this study.

Site	Location (Type)	Network or Data Source	Data
BHM	Birmingham, AL (urban)	SEARCH	Hourly ozone; 24-h & hourly aerosol[1]
CTR	Centreville, AL (rural)	SEARCH	Hourly ozone; 24-h & hourly aerosol[1]
GFP	Gulfport, MS (urban)	SEARCH	Hourly ozone; 24-h & hourly aerosol[1]
JST	Atlanta, GA (urban)	SEARCH	Hourly ozone; 24-h & hourly aerosol[1]
OAK	Oak Grove, MS (rural)	SEARCH	Hourly ozone; 24-h & hourly aerosol[1]
OLF	Outside Pensacola, FL (rural)	SEARCH	Hourly ozone; 24-h & hourly aerosol[1]
PNS	Pensacola, FL (urban)	SEARCH	Hourly ozone; 24-h & hourly aerosol[1]
YRK	Yorkville, GA (rural)	SEARCH	Hourly ozone; 24-h & hourly aerosol[1]
GSM	Great Smoky Mts., TN (rural)	VISTAS/TVA	Hourly ozone; 24-h & hourly aerosol[2]
CCI	Cook County (Chicago), IL (urban)	AIRS/AQS	Hourly sulfate
CLT	Charlotte, NC (urban)	AIRS/AQS	Hourly ozone

[1]Aerosol data include sulfate, nitrate, ammonium, organic carbon, elemental carbon and total $PM_{2.5}$ mass.
[2]Aerosol data include sulfate, nitrate, organic carbon, elemental carbon and total $PM_{2.5}$ mass. Ammonium data were available for 24-h samples only.

Table 2. Summary of observed and modeled ozone.

	Observed[2]			Model[2]			Daytime[3]
Site[1]	Max. OEI / Sector	2nd Highest OEI / Sector	Max. 1-hr Ozone, ppm	Max. OEI / Sector	2nd Highest OEI / Sector	Max. 1-hr Ozone, ppm	Ratio of Mean Obs. to Mean Model O_3
BHM (U)	4.26 / NW	3.27 / N	0.116	2.03 / S	1.75 / SW	0.089	1.07
CTR	4.31 / NW	2.88 / N	0.099	0.18 / NE	0.00 / [4]	0.062	1.23
GFP (U)	5.18 / SW	2.57 / S	0.104	0.48 / N	0.45 / S	0.074	1.09
GSM	7.04 / N	6.80 / SW	0.106	1.05 / N	0.38 / NE	0.074	1.25
JST (U)	6.03 / NW	5.86 / W	0.131	3.37 / S	1.46 / SW	0.111	1.24
OAK	2.24 / SW	1.70 / N	0.089	0.32 / S	0.00 / [4]	0.066	1.13
OLF	3.90 / SW	2.39 / W	0.101	0.06 / SW	0.00 / [4]	0.064	1.06
PNS (U)	2.32 / S	2.16 / W	0.110	0.31 / SW	0.00 / [4]	0.064	1.07
YRK	14.52 / NW	8.08 / N	0.097	3.46 / E	2.29 / SE	0.087	1.14
CLT (U)	1.76/ N	1.01/ SE	0.090	0.56/ NW	0.53/ E	0.072	0.88

[1]A "U" following the site code indicates an urban site.
[2]Ozone exposure index (OEI) expressed as ppm-hours.
[3]Daytime is defined here as the peak hours of ozone, 1000-1800 local time.
[4]Zero OEI was computed for more than one sector.

Table 3. Model versus observed mean 24-hour aerosol concentrations across all sites.

Species	Observed, μg m^{-3}	Model, μg m^{-3}
Sulfate	4.81	5.85
Nitrate	0.28	0.02
Ammonium	1.60	0.88
Organic aerosol[1]	7.22	5.35
Elemental C	0.85	0.36
$PM_{2.5}$	13.2	13.6

[1]Model organic carbon multiplied by 1.8 to approximate total organic aerosol mass.

Table 4. Summary of the direction of origin for the highest and lowest 24-hour aerosol concentrations averaged by wind direction sector for each site.

Particle Species	Data Type	Direction Sector[1]								
		BHM	CTR	GFP	GSM	JST	OAK	OLF	PNS	YRK
Highest										
Sulfate	Observed	N	NW	N	NW	NW	N	W	W	N
	Model	N	N	SW	N	S	N	NE	NW	NW
Ammonium	Observed	N	NW	N	NW	NW	N	W	W	N
	Model	N	N	SW	N	N	N	N	NW	N
Organic	Observed	NE	E	N	NE	N	NE	S	W	N
	Model	W	E	SW	W	N	N	NE	NW	S
Elemental C	Observed	NE	N	[2]	[2]	[2]	NE	[2]	[2]	[2]
	Model	[2]	N	[2]	[2]	N	N	[2]	NW	N
$PM_{2.5}$	Observed	NE	NW	N	NW	N	N	NW	NW	NW
	Model	N	N	N	SW	N	N	NW	NW	S
Lowest										
Sulfate	Observed	SE	SE	S	SE	E	SE	SW	E	SE
	Model	NE	SE	SE	NE	NE	S	S	S	NE
Ammonium	Observed	SE	SE	S	SE	E & S	SE	E	E	SE
	Model	S	SE	SE	NE	E	S	S	S	NE
Organic	Observed	S	SE	S	SE	S	SE	SW	SW	SE
	Model	S	S	SE	NW	E	E	S	S	SW
Elemental C	Observed	SE	SE	[2]	[2]	[2]	SE	[2]	[2]	[2]
	Model	[2]	S	[2]	[2]	E	E & S	[2]	S	SW
$PM_{2.5}$	Observed	S	S	S	SE	E	S	S	SE	SW
	Model	SW	S	SE	NE	E	SE	S	S	SW
Below: total number of sector matches (within one sector) above between model and observations.										
All[3]		6	10	5	2	6	10	4	6	3

[1]Sector that corresponds with the highest or lowest average concentrations and for which 2 or more data points exist.
[2]No significant directional variation.
[3]Maximum possible value per site is 10.

Table 5. Fractional variance shared between hourly modeled and observed aerosol concentrations.[1]

Aerosol Type	Degree of Association: Urban Sites			Degree of Association: Non-urban Sites		
	BHM	JST	CCI	CTR	YRK	GSM
Sulfate	0.00	0.30	0.37	0.48	0.25	0.25
Nitrate[2]	0.56	0.03	N/A	0.11	0.03	0.01
Ammonium	0.40	0.35	N/A	0.49	0.25	N/A
Organic C	0.35	0.39	N/A	0.15	0.18	0.32
Elemental C[2]	0.43	0.12	N/A	0.14	0.02	0.20
Total C	0.49	0.41	N/A	0.19	0.19	0.32
$PM_{2.5}$	0.68	0.44	N/A	0.40	0.13	0.35

[1]N/A = not available. Data were not collected for this site.
[2]Correlations of this species computed using log-transformed concentrations due to large number of extremely low values.

Table 6. Correlated variance fraction of block averages of hourly pollutant concentrations.

Pollutant	Degree of Association: Urban Sites			Degree of Association: Non-urban Sites		
	BHM	JST	CLT[1]	CTR	YRK	GSM
Ozone	0.92	0.62	0.55	0.54	0.68	0.10
$PM_{2.5}$	0.05	0.04	N/A	0.10	0.03	0.00
Sulfate	0.14	0.10	N/A	0.17	0.18	0.01
Total C	0.23	0.01	N/A	0.27	0.01	0.01

[1]N/A = not available. Data were not collected for this site.

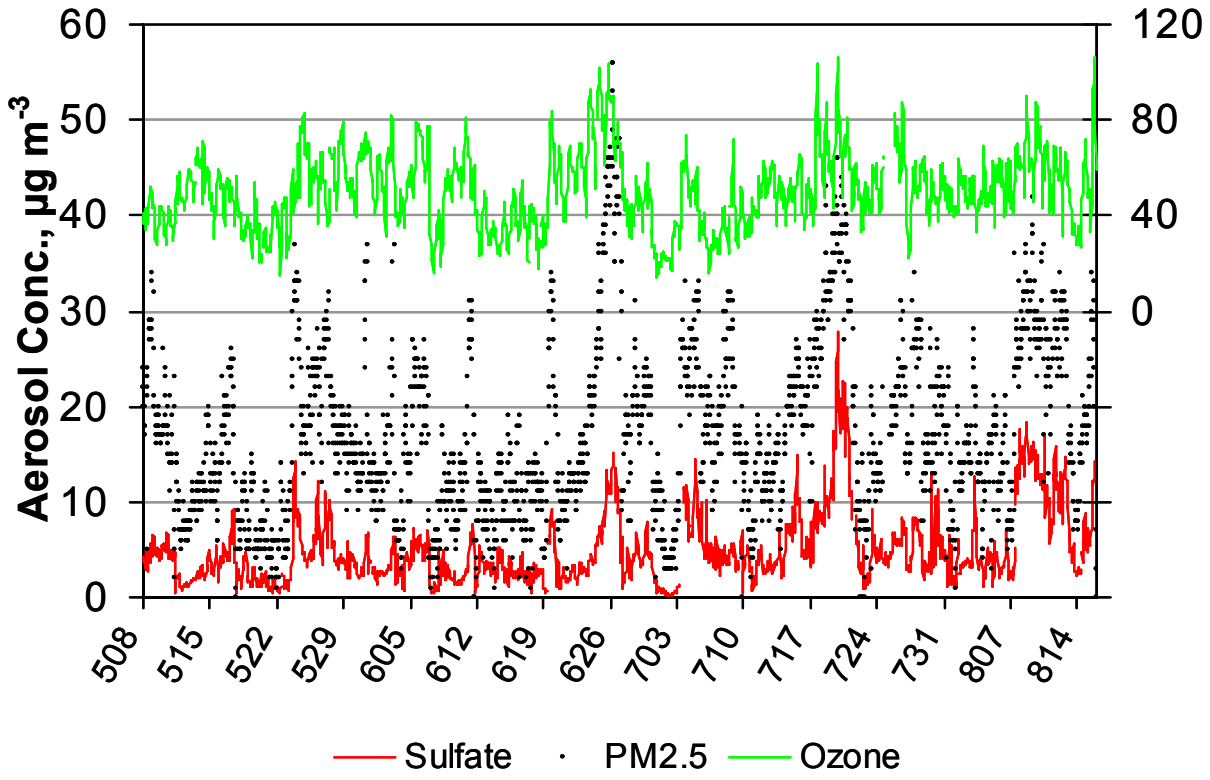

Figure 1. Time series of observed hourly ozone mixing ratio, and sulfate and $PM_{2.5}$ mass concentrations at site GSM (Look Rock, Great Smoky Mountains) in Tennessee. The *x* axis is labeled with three digit numbers representing the month (first digit) and date (digits 2-3). All dates are in 2003.

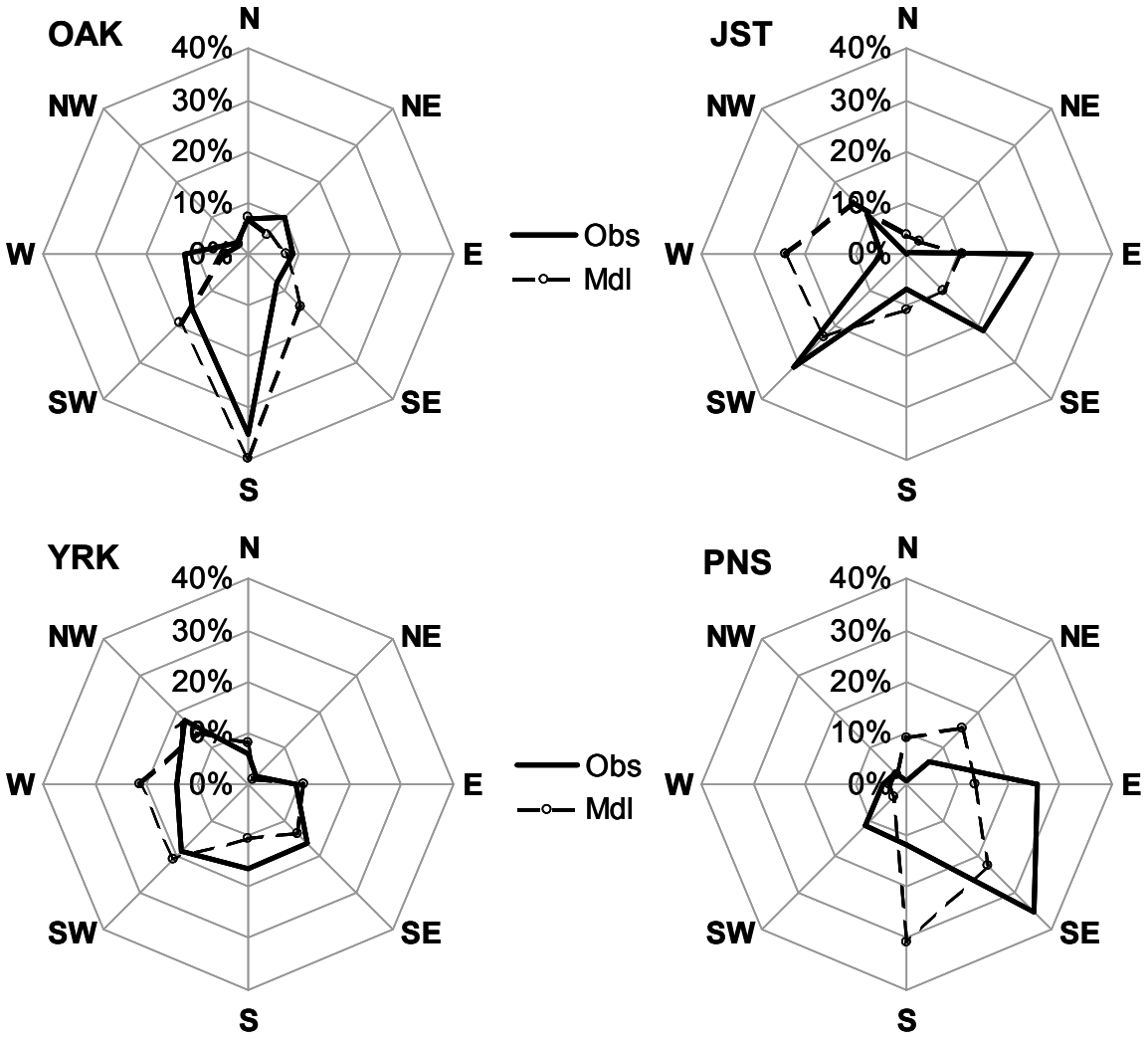

Figure 2. Surface wind roses for selected sites illustrating differences between observations and modeled values when wind speeds >2 m s^{-1}. Data cover the study period of May-August 2003.

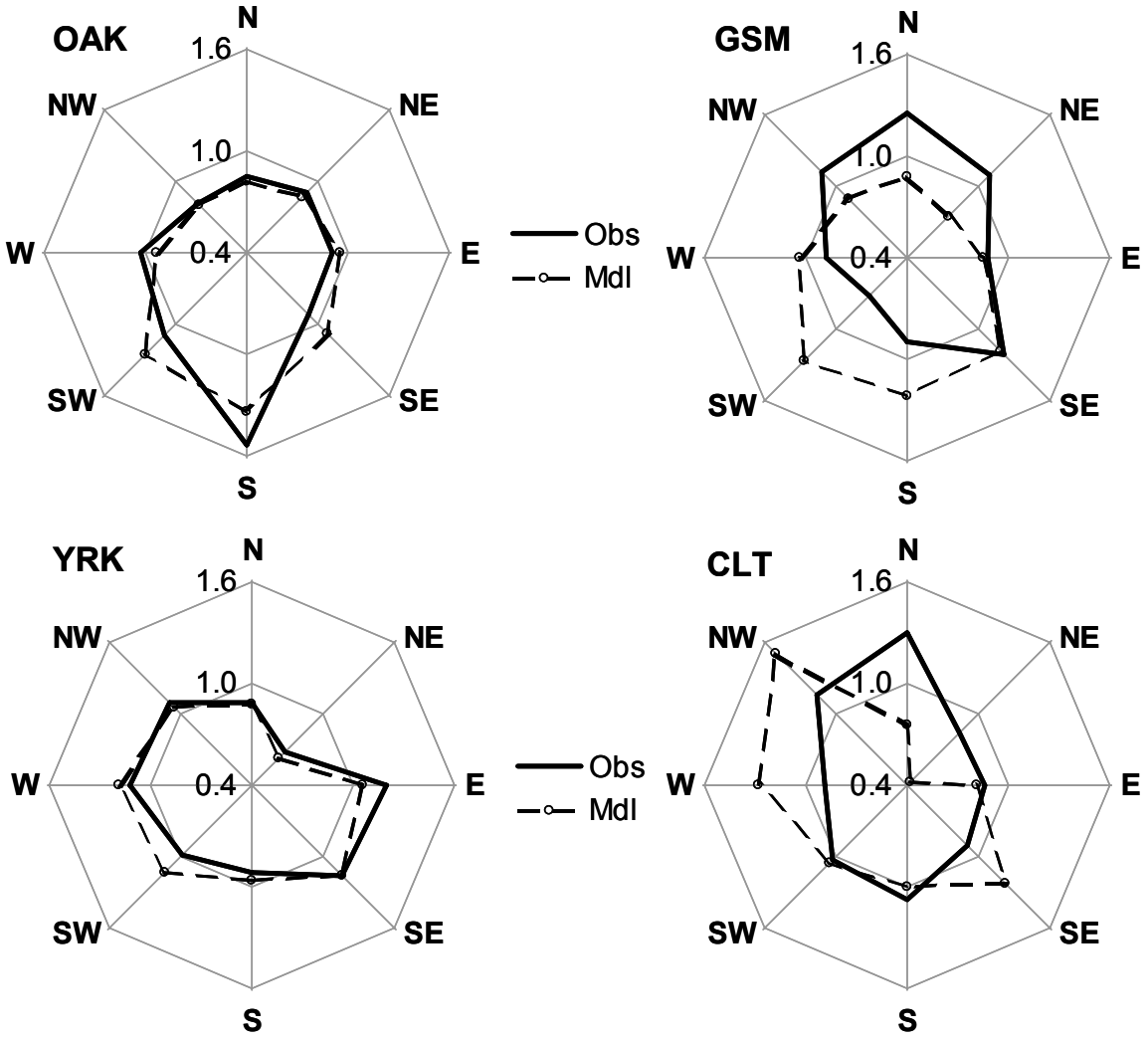

Figure 3. Distribution of observed and modeled relative wind speed (sector speed/overall average speed) by direction for selected air quality monitoring sites. Data cover the study period of May-August 2003. Note that the minimum axis value (at plot center) is 0.4.

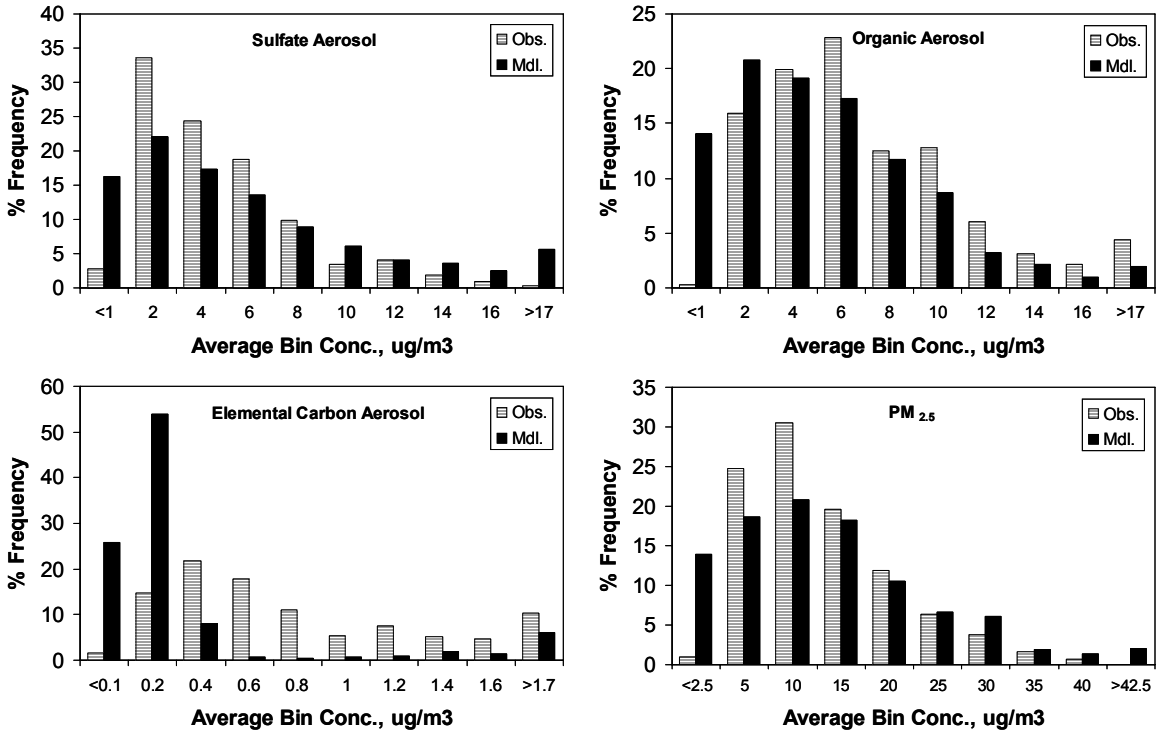

Figure 4. Distributions of observed and modeled 24-h average aerosol concentrations compared across all sites.

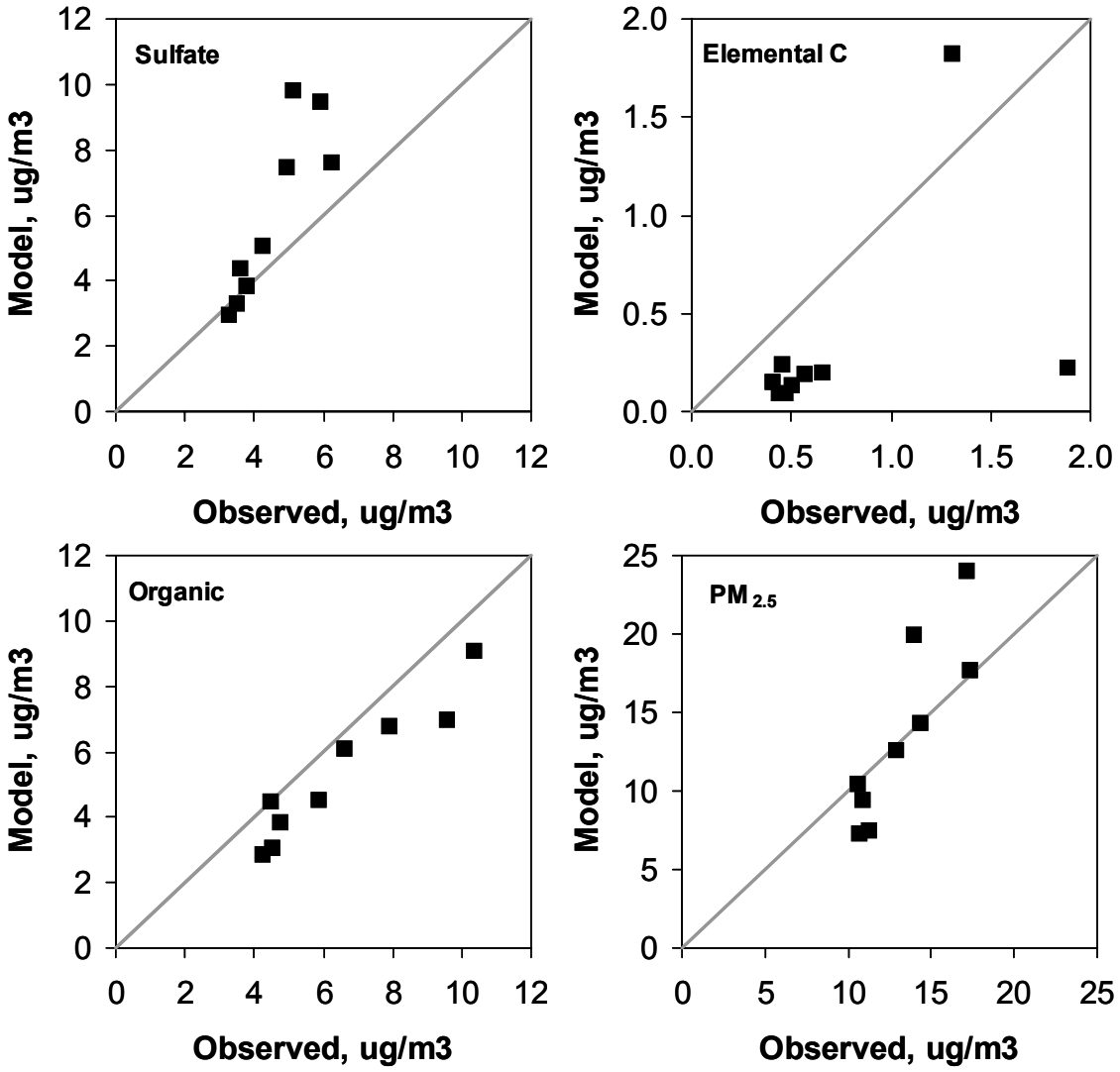

Figure 5. Site average observed and modeled 24-h aerosol concentrations compared.

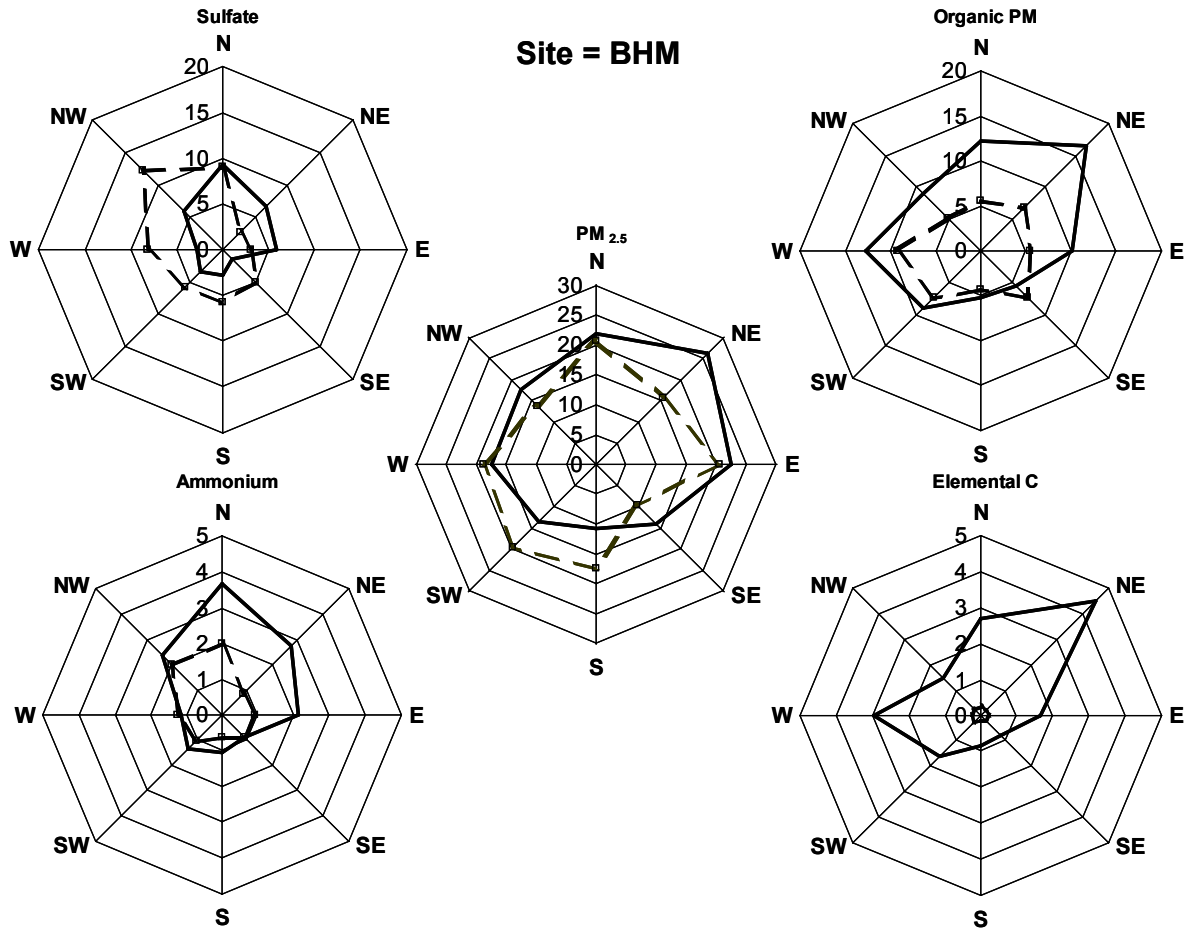

Figure 6. Mean observed (solid line) and modeled (dashed line) 24-h aerosol concentration by daily mean (resultant vector) wind direction for site BHM.

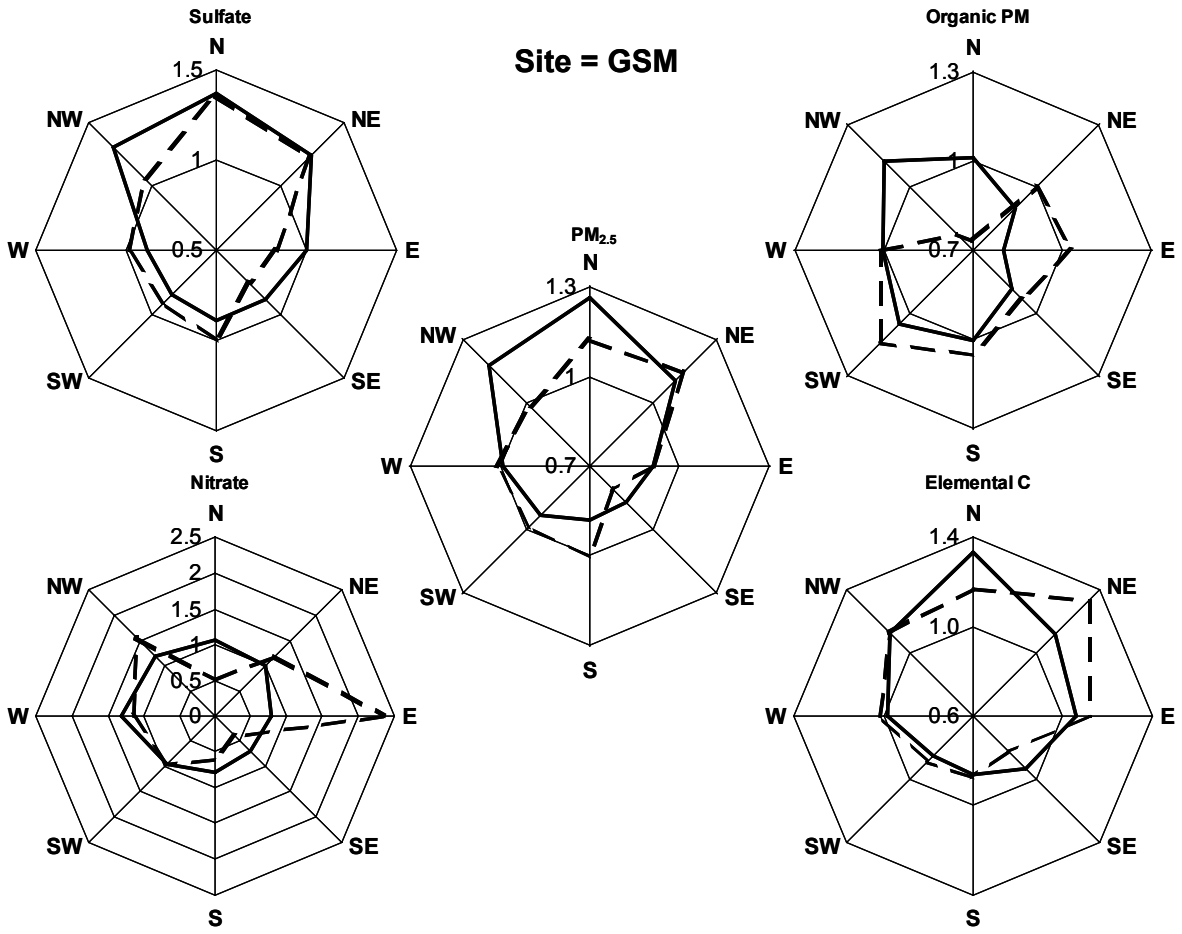

Figure 7. Mean normalized observed (solid line) and modeled (dashed line) hourly aerosol concentration by wind direction for site GSM. Note the variation of axis values at the center for the different plots and the fact that most are not zero.

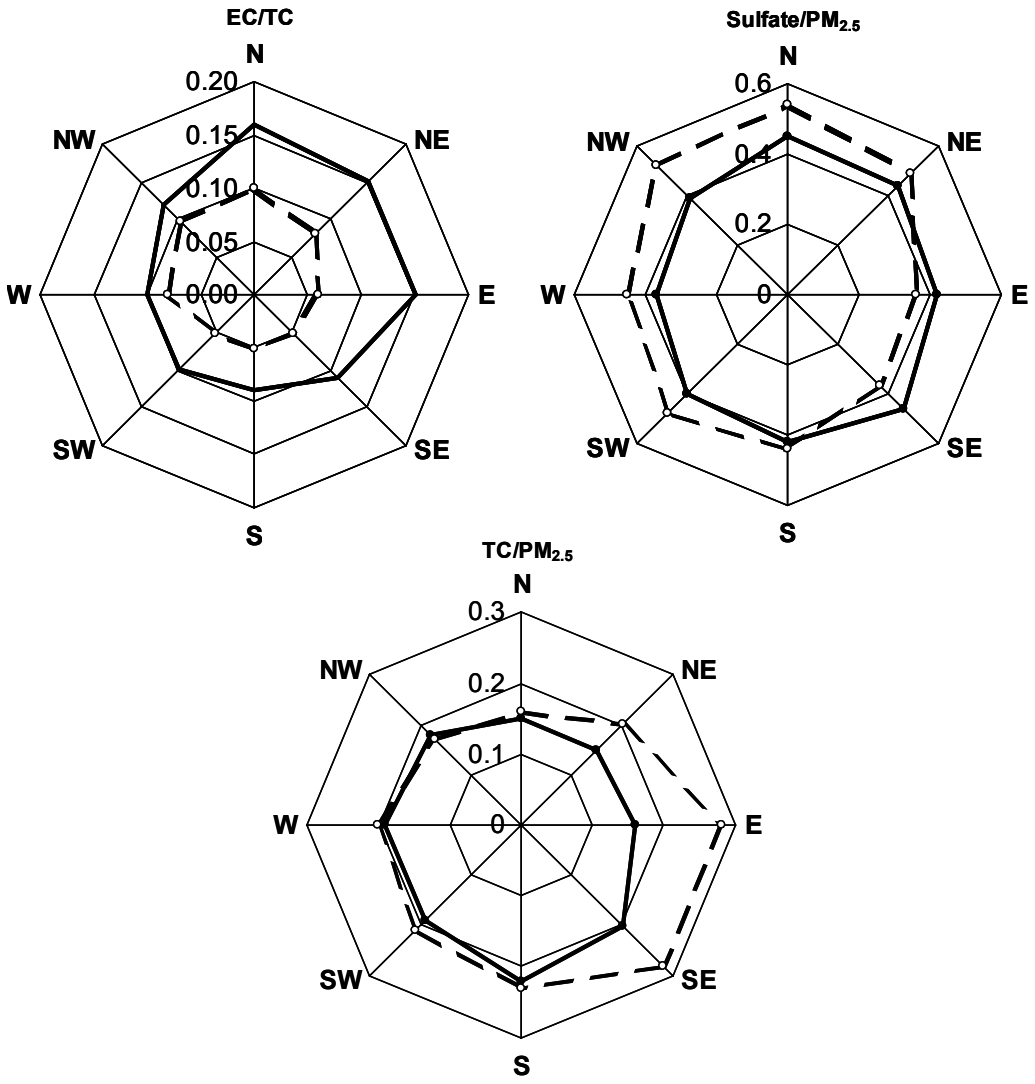

Figure 8. Variations of observed (solid line) and modeled (dashed line) aerosol component ratios averaged by wind direction for site GSM. Ratios were computed from hourly data.

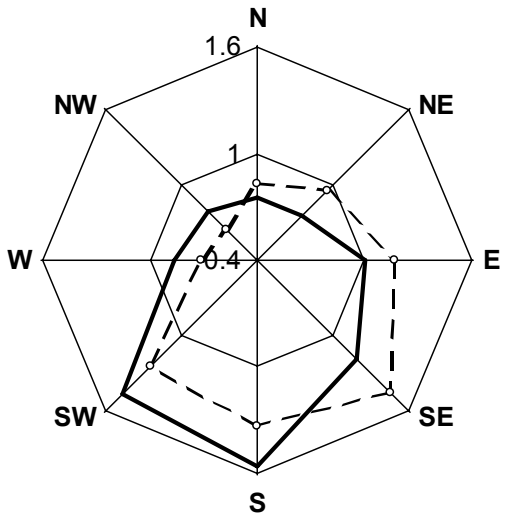

Figure 9. Mean normalized observed (solid line) and modeled (dashed line) hourly sulfate concentration by wind direction for site CCI.

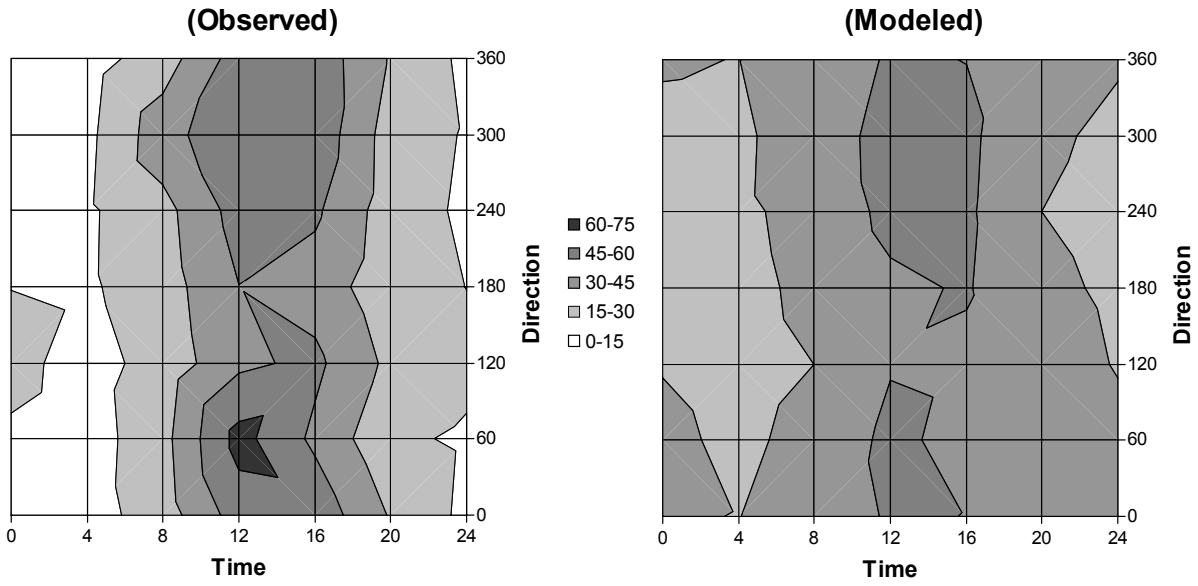

Figure 10. Mean ozone mixing ratio (in parts per billion) as a function of time of day and wind direction for site BHM. Averaging was done for all values within 4-hour time and 60° direction blocks.

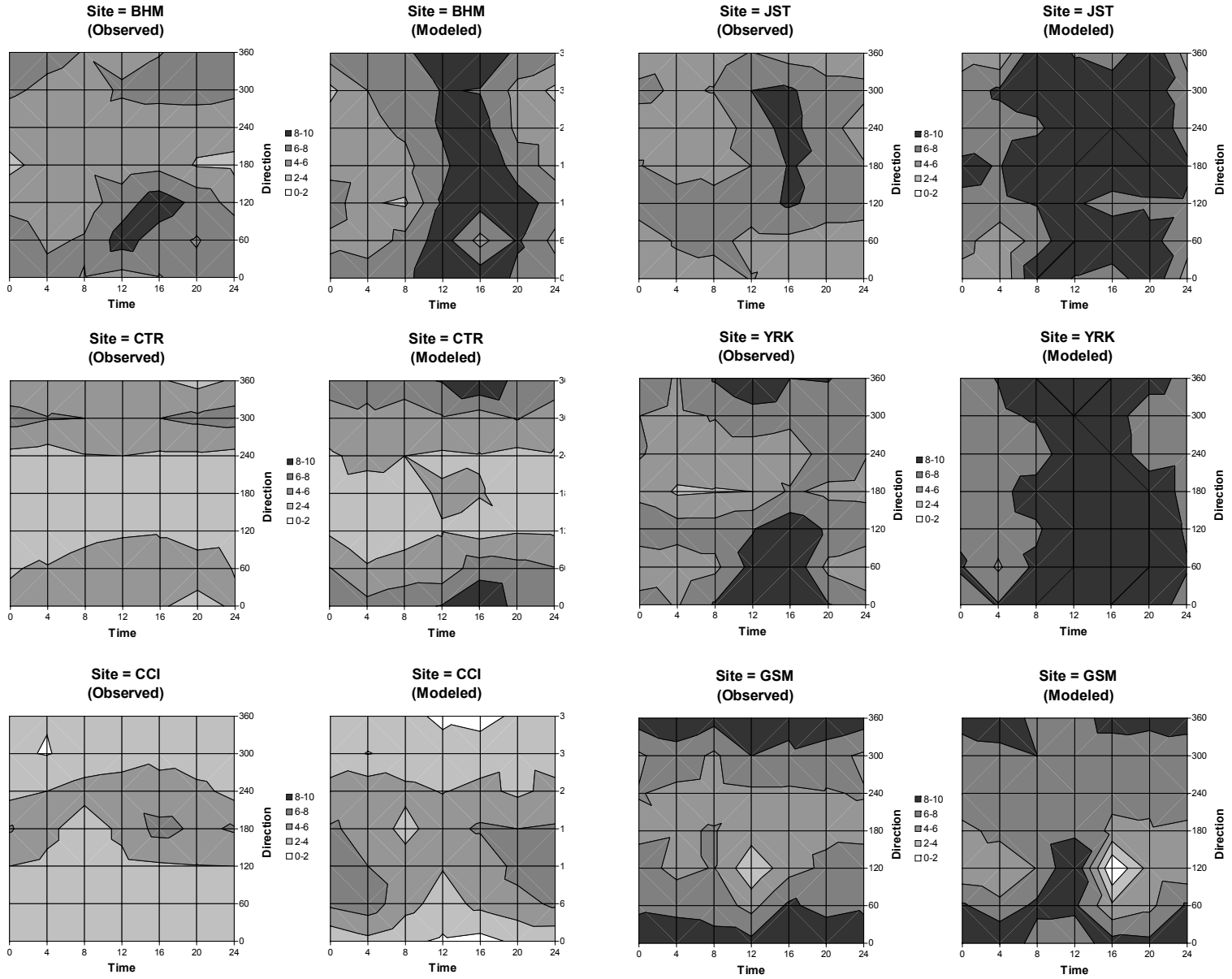

Figure 11. Space-time plots of average observed and modeled sulfate concentration (μg m^{-3}) fields at various sites.

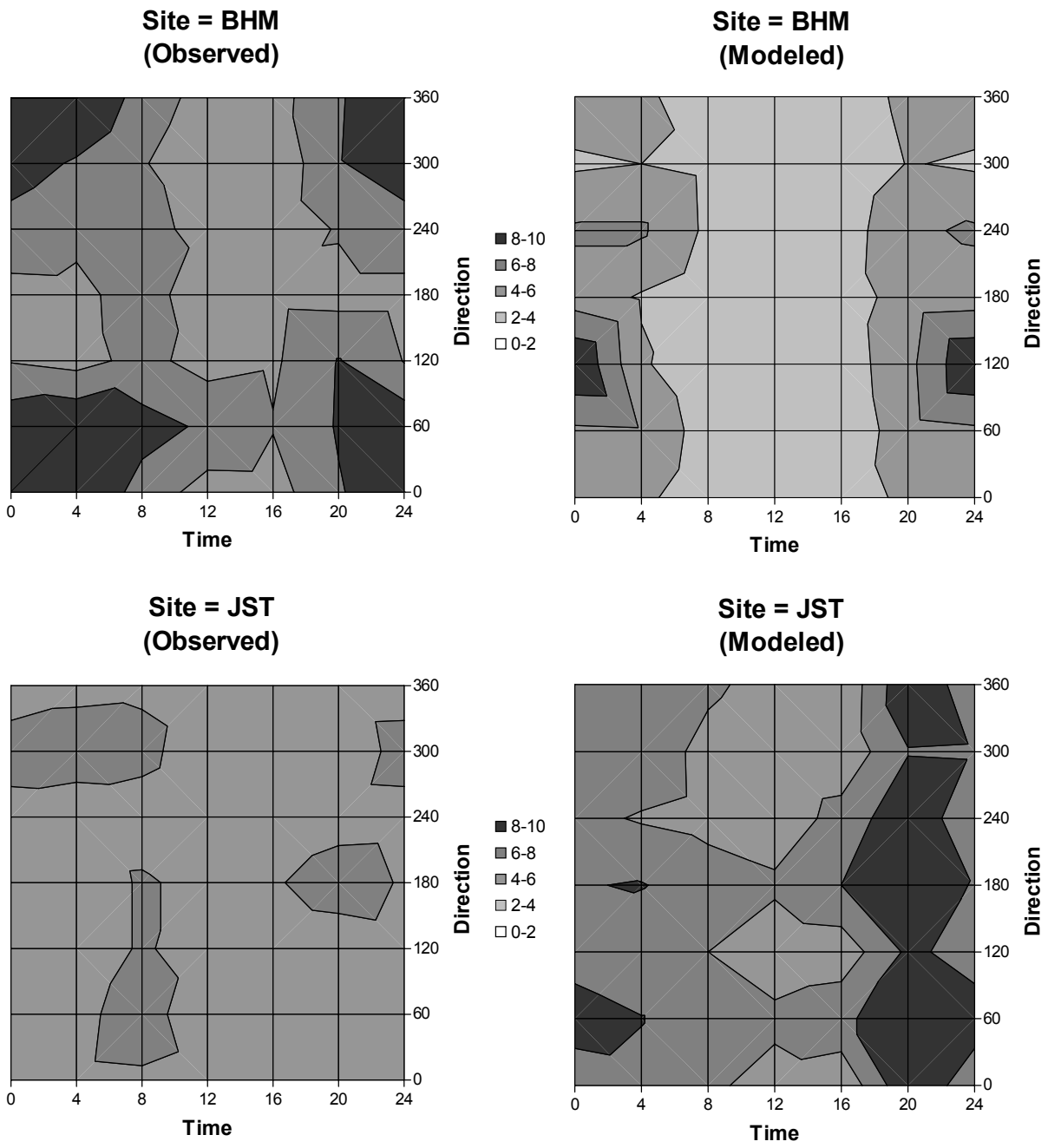

Figure 12. Same as in Figure 11 except for total fine carbonaceous aerosol mass.

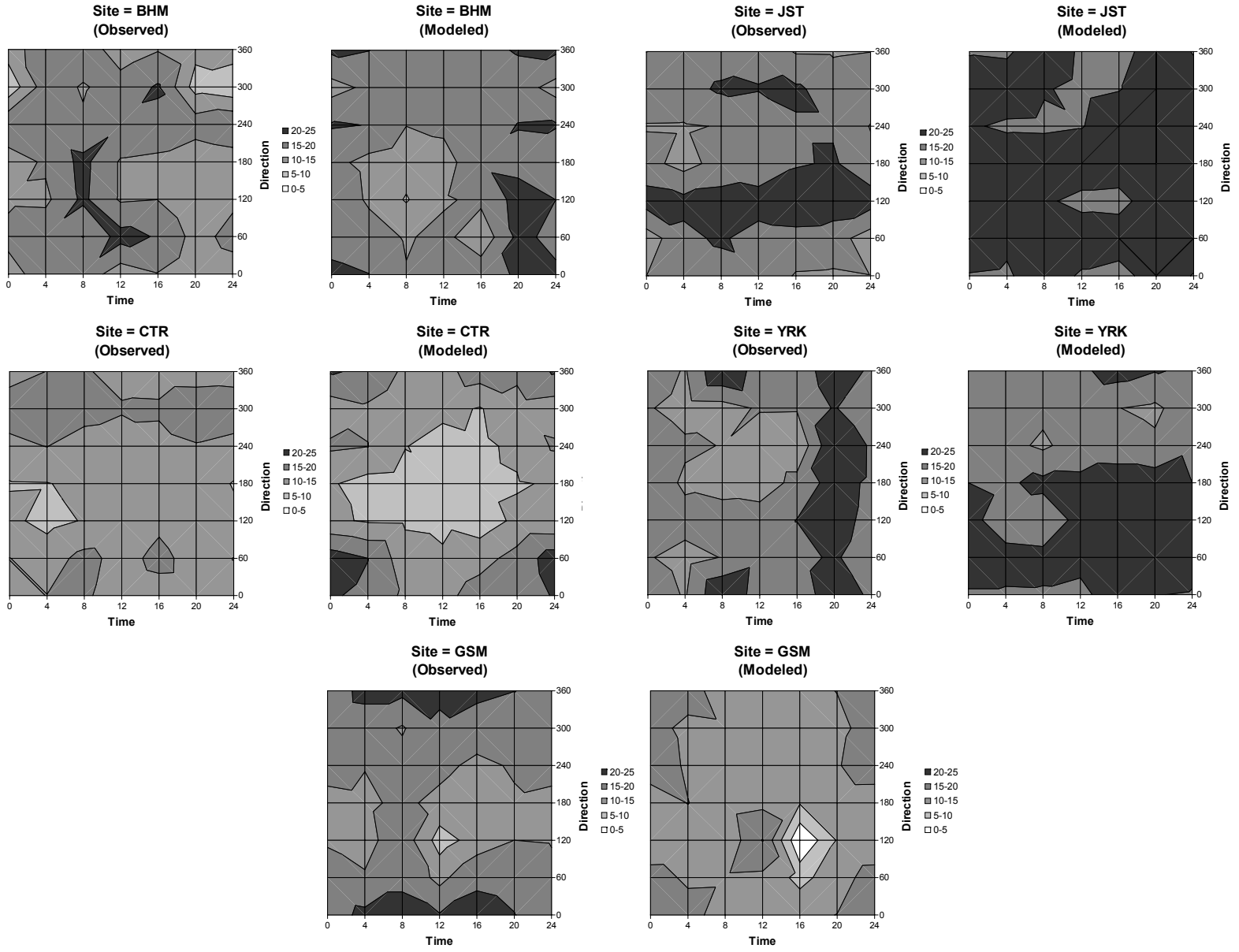

Figure 13. Same as in Figure 11 except for total $PM_{2.5}$ mass.