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Simulations of fine particulate matter ($PM_{2.5}$) in Houston, Texas

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[1] Simulations of fine particulate matter ($PM_{2.5}$) during an eight-day episode (24 to 31 August 2000) is conducted in association with the 2000 Texas Air Quality Study (TexAQS 2000) and the Houston Supersite Project using the EPA's Models-3 Community Multiscale Air Quality model (CMAQ). The mass concentrations of $PM_{2.5}$ and major chemical constituents during the episode are calculated and compared with available field measurements. The predicted daily $PM_{2.5}$ mass concentrations are about 8.5–13.0 $\mu g/m^3$, consistent with the observed values. The diurnal patterns of $PM_{2.5}$ mass concentrations are similar throughout the region, with a strong morning peak and a weak peak in the late afternoon to the early evening. High primary emissions, high formation rates of the secondary fine particulate matter, and low planetary boundary layer (PBL) heights contribute to the morning peak. The major components of the fine particulate matter in this region are sulfate, organic carbon, elemental carbon and ammonium. The model predicts about 30% sulfate, 32% organics (including elemental carbon (EC)), and 10% ammonium of the total $PM_{2.5}$ mass. The balance of the primary cations and anions indicates that fine particulate matter in this region is acidic. Comparison with field observation reveals that CMAQ produces good simulations of averaged daily mass concentrations of major components such as sulfate, organic carbon, elemental carbon and ammonium with normalized mean biases (NMB) of less than ±25%. Uncertainties in the aerosol precursor emissions, the aerosol chemistry especially about secondary organic aerosol (SOA) formation and aqueous reactions, and the calculated PBL heights are likely responsible for the differences.

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1. Introduction

[2] Aerosols or fine particulate matter, $PM_{2.5}$, in the atmosphere have been of great interest in recent years [*Environmental Protection Agency* (*EPA*), 1996, 2000; *Zhang et al.*, 2004a]. Concerns over human health effects of fine particulate matter constitute the most important element in formulating the national ambient air quality standard [*EPA*, 1996]. High levels of particulate matter are believed to be associated with adverse human effects, including increased morbidity and mortality arising from altered respiratory and cardiovascular function. Aerosols directly or indirectly affect the Earth's energy balance [*Charlson et al.*, 1987; *Intergovernmental Panel on Climate Change*, 2001]. The aerosol direct effect occurs under clear-sky conditions by scattering or absorbing solar radiation. The aerosol indirect effect takes place by increasing cloud particle concentrations and enhancing cloud reflection of solar radiation. The indirect effect on the energy budget is also related to the earth hydrological cycle, since a smaller particle size is unfavorable for growth of cloud particles to raindrops and hence inhibits precipitation and prolongs the lifetime of the cloud [*Orville et al.*, 2001]. Modification of cloud and precipitation by aerosols may enhance lightning activity and thus influence tropospheric chemistry [*Orville et al.*, 2001; *Zhang et al.*, 2003]. Furthermore, aerosols contribute to regional acid deposition and visibility degradation [*EPA*, 1996, 2000], and promote multiphase chemical processes [*Zhang et al.*, 1993a, 1993b; *Zhang and Leu*, 1997; *Zhao et al.*, 2005].

[3] Unlike ozone which is being treated a single pollutant [*Lei et al.*, 2004; *Zhang et al.*, 2004b], $PM_{2.5}$ consists of mixtures of various chemical components and over a wide size distribution resulting from physical and chemical processes that make $PM_{2.5}$ a difficult pollutant to model. Modeling of particulate matter is complicated because of the lack of adequate measurements for comparison. Recently, hourly $PM_{2.5}$ measurements with Tapered Element Oscillating Microbalance (TEOM) and Federal Reference Method (FRM) during the Houston Supersite Project provide valuable data to evaluate modeling results in

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southeast Texas [*Allen*, 2002; *Russell et al.*, 2004]. Recent studies and regulatory modeling suggest that the urban and industrial areas in Houston may be close to exceeding the proposed National Ambient Air Quality Standards (NAAQS) for $PM_{2.5}$, which is 15 $\mu g/m^{-3}$ for the annual average concentration [*Allen*, 2002; *Tropp et al.*, 1998]. Measurements of $PM_{2.5}$ in southeast Texas show that in the industrial area of Houston, the Ship Channel, the measured average $PM_{2.5}$ mass has been above the annual average standard [*Tropp et al.*, 1998]. Analyses of TEOM and FRM measurements also show that the average $PM_{2.5}$ is close to NAAQS and the major components of $PM_{2.5}$ are organics and sulfate, both comprising ~30% of the fine particulate matter mass in southeast Texas [*Allen*, 2002; *Russell et al.*, 2004]. The mass concentrations and compositions of the fine particulate matter are spatially homogeneous in the region. A strong morning peak in $PM_{2.5}$ mass concentrations is observed throughout the region and a weak and slightly less consistent peak is observed in the late afternoon to early evening [*Allen*, 2002; *Russell et al.*, 2004]. The study also reveals that the aerosol is slightly acidic and much of the carbonaceous material is due to secondary organic aerosol formation [*Allen*, 2002; *Russell et al.*, 2004].

[4] Air quality models such as the EPA's Models-3 Community Multiscale Air Quality model (CMAQ), are useful tools to assess the current and further air quality regulations to protect human health and welfare [*Mebust et al.*, 2003]. Models-3/CMAQ is a third-generation air quality modeling and assessment tool designed to support air quality modeling applications ranging from regulatory issues to science inquiries on atmospheric science processes [*EPA*, 1999]. The CMAQ aerosol component, or module, designed to simulate the complex processes involving PM, is derived from the Regional Particulate Model (RPM) [*Binkowski and Shankar*, 1995], an extension of the Regional Acid Deposition Model (RADM) [*Chang et al.*, 1991]. The aerosol species considered within the CMAQ aerosol module include sulfate, nitrate, ammonium, water, primary organic aerosol, secondary organic aerosol of both anthropogenic and biogenic origins, elemental carbon, primary material not otherwise specified and wind-blown dust [*Binkowski and Roselle*, 2003]. Two different modes, the Aitken and accumulation modes, each having variable standard deviations, represent $PM_{2.5}$ particles in the CMAQ aerosol module. Conceptually, the Aitken mode represents fresh particles resulting from nucleation and/or direct emissions. The accumulation mode denotes aged particles. Detailed descriptions of the algorithms of this module have been presented previously [*Binkowski and Roselle*, 2003; *Jiang and Roth*, 2003]. The model performance for visibility and speciated aerosol such as organic carbon, sulfate and nitrate has been evaluated against observations [*Eder et al.*, 2000; *Mebust et al.*, 2003].

[5] In this study, we have simulated $PM_{2.5}$ using the Models-3/CMAQ for a period associated with the Texas Air Quality Study 2000 (TexAQS 2000) and the Houston Supersite Project to investigate the characteristics of fine particulate matter in Houston and to evaluate the model performance on aerosol simulations. The model results are compared to PM2.5 measurements with TEOM and FRM during the Houston Supersite Project [*Allen*, 2002; *Russell et al.*, 2004].

2. Methods

[6] The model domain was comprised of 60 × 60 Lambert Conformal grids encompassing an area of 57,600 km^2 with a 4-km resolution centered at 29.83 N and 95.05 W. The horizontal grid specification of the domain followed that of the 4-km MM5 meteorological grids, except removing the outer 35 horizontal rows of MM5 grid points to reduce the boundary effects. There were 21 layers in the vertical direction from the surface to the top, identical to those of gridded emission data. Initial and boundary conditions were generated from the CMAQ simulation results with 12-km horizontal resolution and 45 × 45 grid cells centered at 30.04°N and 95.72°W, using CMAQ initial condition (ICON) and boundary condition (BCON) processors.

[7] The meteorological fields for chemical transport simulations were generated during TexAQS 2000 by J. W. Nielsen-Gammon (Meteorological modeling files, 2003, available at http://www.tnrcc.state.tx.us/air/aqp/airquality_photomod.html#met) using MM5, which incorporated wind profiler and GOES satellite data. The MM5 output files were post-processed for the model domain by EPA's Models-3 Meteorology-Chemistry Interface Processor Version 2.2 (MCIP2). During the processing, vertical layer collapsing was performed to reduce the vertical layers from 43 sigma levels (42 vertical layers) to 22 sigma levels (21 vertical layers) for alleviating the computational costs associated with a larger number of vertical layers.

[8] The emission inventory used in this study was from EPA's National Emission Inventory (NEI99) final version 3. The raw NEI99 data were converted into the Inventory Data Analyzer (IDA) and processed using Sparse Matrix Operator Kernel Emissions (SMOKE) Modeling System Version 1.5β by *Lin et al.* [2002] to obtain the gridded emission inventory data sets, ready for CMAQ runs. The Houston region contains a mix of major sources of ozone and SOA precursors. Houston is the tenth largest metropolitan area in the United States, and hosts one of the world largest petrochemical complexes and several large fossil-fueled electric power plants. Transportation and industry emit a great quantity of VOCs, NO_x, and SO_2. In particular, the Houston Ship Channel region, east of the city center, represents major high emission sources of VOCs from petrochemical plants [*Lei et al.*, 2004; *Zhang et al.*, 2004b], which are believed to the major contributor to ozone and SOA formation in this region [*Daum et al.*, 2003]. It is known that NEI99 inventory underestimated emissions of VOCs [*Lin et al.*, 2002]. Compared with the emission inventory data with modified olefin emissions used for CAMx (Comprehensive Air Quality Model with extension) simulations provided by Texas Commission for Environmental Quality (TCEQ), the emission quantities of olefins in NEI99 data are about 3–10 times smaller in the southeast of Texas. Therefore we increased the olefin emissions to 8 times of the original quantities in this study in order to more accurately represent VOC emissions in this area. Also, because of the very low aromatic hydrocarbon emissions reported in NEI99 data and much uncertainty

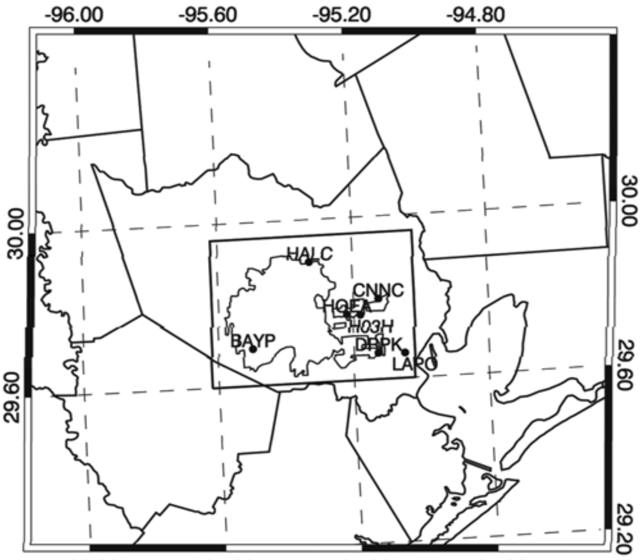

Figure 1. Study domain and PM monitoring sites in the Houston area.

about the emissions of aromatics in Houston [*Karl et al.*, 2003], the emissions of aromatics such as toluene and xylenes were also boosted by 8 times.

[9] CMAQ Version 4.3 was employed in this study, which has major modifications on the treatment of secondary organic aerosol (SOA) formation and the heterogeneous N_2O_5 reaction probability [*EPA*, 2003]. The chemical mechanism chosen in this study was RADM2 with aqueous chemistry extension. The aerosol module AERO3 was used, representing the newest version released in 2002. Schell algorithm was used to calculate the secondary organic aerosol (SOA) formation rate [*Schell et al.*, 2001]. Both the Aitken and accumulation modes contributed to the $PM_{2.5}$ number concentrations. We presented in this work only the mass concentration of $PM_{2.5}$, which is mainly contributed by the accumulation mode. Also, there were few measurements of new particle formation during this episode. The Modified Euler Backward Interactive (MEBI) gas-phase chemistry solver was used for the RADM2 chemical mechanism. The Models-3/CMAQ model system was built on Linux platform using Portland Group FORTRAN 90 (PGF90) compilers.

[10] The selected simulation period runs from 24 to 31 August 2000, corresponding to an 8-day episode associated with the TexAQS 2000 and Houston Supersite Project. This period corresponds to typical summertime emissions and meteorological conditions in this region. This episode had two distinct meteorological regimes in the Houston area. From 25 to 29 August, the wind was predominantly southeasterly. In contrast, the wind was predominantly westerly on 30 and 31 August. During 25 August, a large-scale wind of close to 3 m s^{-1} led to a few hours in which coastal circulation caused the wind to become calm and gradually reverse. No stagnation events were seen during the next 4 days since the large-scale wind was slightly stronger. The temperature distribution during 25 to 29 August did not change significantly. The Houston area was essentially cloud-free with the exception of a few isolated showers on 26 and 29 August. On 28 August the sky was cloudy but without showers. The composite of winds showed little vertical wind shear during this period. On 30 and 31 August, the Houston area was characterized with high temperatures and light winds in the afternoon (near-stagnation). Instead of the similar wind variations with height, the diurnal cycle decayed to near zero by a height of 1 km; and instead of wind variation of a few meters per second, the wind changed by more than 10 m/s on average between sunset and sunrise [*Nielsen-Gammon*, 2001, 2002]. The MM5 results employed in this study reasonably reproduced the sea breeze circulation and urban heat island effect characteristic of this region, with an overall root-mean square accuracy of about 15 m/s [*Lei et al.*, 2004; *Nielsen-Gammon et al.*, 2005].

Table 1. Descriptions of the PM Monitoring Sites in the Study Domain

Abbreviation	Site Descriptions	Latitude	Longitude
CNNC	Channelview C15/C115	29.803	−95.126
DRPK	Houston Deer Park 2 C35/139	29.670	−95.129
BAYP	Houston Bayland Park C53/C146/C181	29.696	−95.499
HOEA	Houston East C1	29.768	−95.221
HALC	Houston Aldine C8/C108/C150	29.901	−95.326
H03H	HRM-3 Haden Road C603/C114	29.765	−95.181
LAPO	La Porte Airport during TexAQS	29.667	−95.050

[11] The study domain in Houston covered the latitude from 29.60°N to 29.96°N and longitude from 95.62°W to 95.02°W (the box in Figure 1), since the relatively higher $PM_{2.5}$ mass concentrations above the annual average standard frequently occurred in this area. In addition, PM monitoring sites were concentrated in this area, which was ideal for the model evaluation by comparing with the observations. Figure 1 shows the locations of the sites for TEOM and FRM measurements within the study domain. The site descriptions are summarized in Table 1: Except for two urban sites (HALC and BAYP), most of the aerosol monitoring stations are located near the industrial Ship Channel region.

3. Results and Discussion

[12] The diurnal variation of ground-level $PM_{2.5}$ mass concentrations averaged over the study domain and over eight simulated days is depicted in Figure 2. A strong maximum

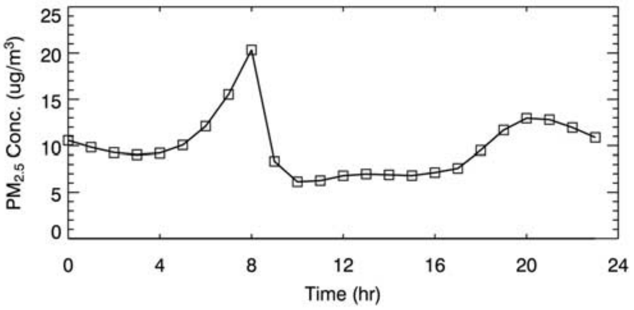

Figure 2. Simulated $PM_{2.5}$ mass concentrations averaged over the study domain and the episode.

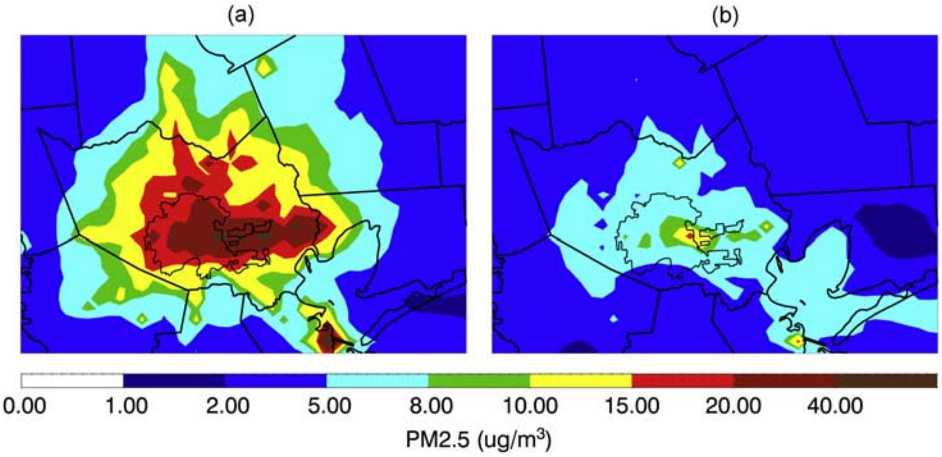

Figure 3. Geographical distribution of simulated $PM_{2.5}$ concentrations at (a) 8:00 am and (b) 3:00 pm averaged during the episode. The time corresponds to the local time or central daylight time (CDT).

with the highest concentration about 21.0 $\mu g/m^3$ occurred around 8:00 am, and a weaker maximum (13.0 $\mu g/m^3$) took place around 8:00 pm. The average hourly $PM_{2.5}$ mass concentrations from 6:00 am to 9:00 am (morning maximum) were slightly above the NAAQS annual average standard, 15.0 $\mu g/m^3$. The temporal variation of $PM_{2.5}$ at different locations was consistent throughout the region. A slight difference (less than 10%) of $PM_{2.5}$ mass concentrations between the weekdays and weekend indicated that the traffic sources did not significantly contribute to the aerosol concentrations in Houston.

[13] The geographic distributions of $PM_{2.5}$ mass concentrations at 8:00 am and 3:00 pm (local time) averaged over the episode in Houston are displayed in Figure 3a and Figure 3b, respectively. At 8:00 am, a morning peak occurred with the $PM_{2.5}$ mass concentration exceeding 15.0 $\mu g/m^3$ (Figure 3a). Especially in and around the Houston urban center and the Ship Channel, the $PM_{2.5}$ mass concentrations were higher than 20.0 $\mu g/m^3$. Along the periphery of Houston, tongues of relatively high $PM_{2.5}$ concentrations were located within major roadways. The model captured localized events with the $PM_{2.5}$ mass concentrations greater than 40.0 $\mu g/m^3$ in and around the Ship Channel. Those localized events have been observed frequently at the monitoring sites located in this area and they were important in determining compliance with the NAAQS. At about 3:00 pm, the $PM_{2.5}$ concentration reached the lowest value during the day. The geographic distribution at this time showed similar patterns to those of the morning maximum, except the absolute $PM_{2.5}$ mass concentrations were much lower (see Figure 3b). The entire area in Houston had $PM_{2.5}$ mass concentrations of about 5.0–8.0 $\mu g/m^3$. $PM_{2.5}$ concentrations were relatively higher (8.0–15.0 $\mu g/m^3$) in the locations near the Ship Channel plumes, owing to formation of secondary fine particulate matter such as sulfate and organics. Therefore the emission sources from the power plants and petrochemical plants contributed significantly to the high $PM_{2.5}$ concentrations in this area. It is clear from Figure 3 that the ratio of $PM_{2.5}$ mass concentrations in the urban to the surrounding rural area is generally greater than 10, indicating that regional transport of $PM_{2.5}$ from the surrounding region is minimal

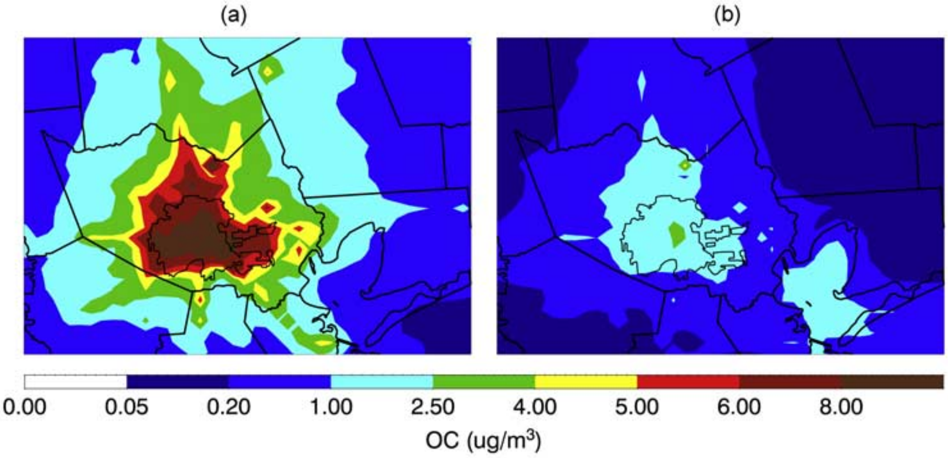

Figure 4. Similar to Figure 3 except for geographical distribution of averaged OC concentrations.

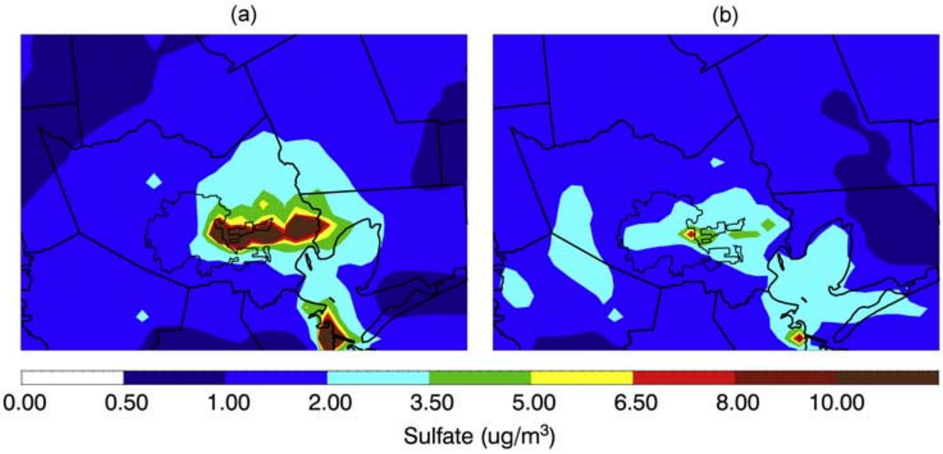

Figure 5. Similar to Figure 3 except for geographical distribution of averaged sulfate concentrations.

compared to the $PM_{2.5}$ production from urban and industrial sources in Houston.

[14] Organic carbon (OC) and sulfate are the most major components of fine particulate matter in the Houston area [*Allen*, 2002; *Russell et al.*, 2004]. The time-averaged geographic distributions of OC and sulfate are shown in Figures 4 and 5, respectively. OC and sulfate have similar geographic distributions as those of $PM_{2.5}$ shown in Figure 3. At 8:00 am, the entire region encountered a relatively high concentration of organic carbon over 5.0 $\mu g/m^3$. Higher organic carbon concentrations (greater than 8.0 $\mu g/m^3$) were predicted in and around the Houston urban center and Ship Channel (Figure 4a). At 3:00 pm, the concentration of organic carbon was low with the value of about 1.0–2.5 $\mu g/m^3$ (Figure 4b). Compared to organic carbon, sulfate was less spatially homogeneous. High sulfate mass concentrations occurred in and around Ship Channel, with the values of over 8.0 $\mu g/m^3$ at 8:00 am and over 3.5 $\mu g/m^3$ at 3:00 pm (Figures 5a and 5b). Point sources burning sulfur-containing fuels around this area were likely responsible for this inhomogeneity.

[15] The averaged $PM_{2.5}$ mass composition is presented in Figure 6. Sulfate, organic carbon, elemental carbon and ammonium are the major constituents of $PM_{2.5}$ in the Houston area. Sulfate consists of about 30% of the total average $PM_{2.5}$ mass. Organic carbon and elemental carbon makes up about 32% of the total $PM_{2.5}$ mass. Ammonium and nitrate account for about 10% and 1% of the total $PM_{2.5}$ mass, respectively. The unspecified component is predicted to be 27% by the model.

[16] The comparisons against FRM measurements were made for the sites where the composition data were available. Table 2 shows that the comparisons between modeled and observed mass concentrations of the major constituents of $PM_{2.5}$ for six sites. The mass concentrations of each component shown in this table are averaged over the days when the measurements are available. Table 2 reveals that the simulated mass concentrations of the components are in good agreement with the observations except for nitrate. For organic carbon, sulfate, elemental carbon, and ammonium, the mean biases are −0.51, −0.87, 0.04, and 0.23 $\mu g/m^3$, respectively; the corresponding normalized mean biases (NMB) are −17.4%, −20.76%, 9.06%, and 24.20%. Those values are less than ±25%, indicating good agreement. The simulated concentrations of organic carbon and sulfate are 0.51 and 0.87 $\mu g/m^3$ less than the measurements, respectively. The mean bias for nitrate is −0.21 $\mu g/m^3$ and the NMB value is −61.46%, indicating a significant underestimation for nitrate. The underprediction by the model with respect to nitrate may be explained by low ammonia emissions in the summer conditions based on the NEI99 [*Mebust et al.*, 2003].

[17] Averaged over the seven monitoring sites in Houston, the daily $PM_{2.5}$ mass concentrations are about 8.5–13.0 $\mu g/m^3$, in agreement with the TEOM observed values, 8.0–14.0 $\mu g/m^3$. The modeled hourly $PM_{2.5}$ mass concentrations were compared with the available TEOM measurements. There were only three sites with the hourly $PM_{2.5}$ data within the study domain, i.e., CNNC, DRPK and HOEA. Figure 7 presents the comparisons of modeled hourly $PM_{2.5}$ mass concentrations averaged over the simulation period against the measurements for the three sites. Generally, the model simulations of hourly $PM_{2.5}$ concentrations were reasonable compared with the observations. The model reproduced the diurnal varia-

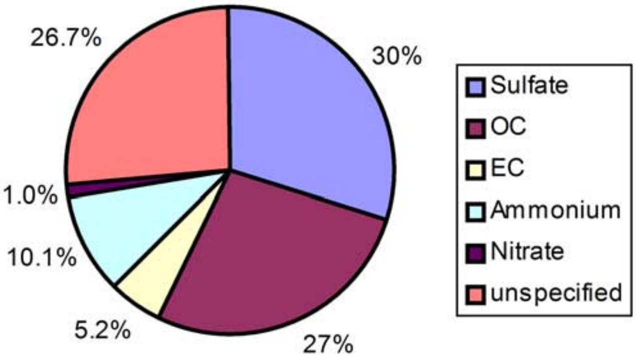

Figure 6. Chemical compositions of simulated $PM_{2.5}$ in the Houston area averaged over the study domain and the episode.

Table 2. Site-by-Site Comparisons of the Major Components of PM$_{2.5}$ Between Modeled and Observed Values

	OC, μg/m^3		Sulfate, μg/m^3		Nitrate, μg/m^3		EC, μg/m^3		Ammonium, μg/m^3	
Sites	Observ.	Model	Observ.	Model	Observ.	Model	Observ.	Model	Observ.	Model
CNNC	3.00	2.20	4.05	5.02	0.22	0.11	0.46	0.45	0.86	1.08
BAYP	2.50	3.03	3.59	1.79	0.34	0.12	0.32	0.62	0.64	0.60
DRPK	2.50	2.02	4.08	2.33	0.36	0.10	0.34	0.39	0.73	0.76
H03H	3.74	3.04	4.95	5.37	0.40	0.14	0.61	0.59	1.04	1.80
LAPO	2.45	1.70	4.33	2.70	0.39	0.09	0.40	0.35	0.80	0.98
HALC	3.88	3.00	4.10	2.68	0.30	0.19	0.58	0.56	0.75	0.96
Mean	3.01	2.50	4.18	3.32	0.34	0.13	0.45	0.49	0.80	1.03
	OC, μg/m^3		Sulfate, μg/m^3		Nitrate, μg/m^3		EC, μg/m^3		Ammonium, μg/m^3	
Mean bias	−0.51		−0.87		−0.21		0.04		0.23	
Normalized mean bias, %	−17.40		−20.76		−61.46		9.06		24.20	

tions, although the predicted peak time was about 1–2 hour later than the observed. The model overpredicted the morning peaks and underestimated the PM$_{2.5}$ concentrations in the afternoon for all sites. Figure 8 presents the diurnal variations of the primary emitted PM$_{2.5}$ and the calculated planetary boundary layer (PBL) heights averaged over the monitoring sites and simulation period. In the early morning (about 8:00 am), the primary emitted PM$_{2.5}$ concentration was

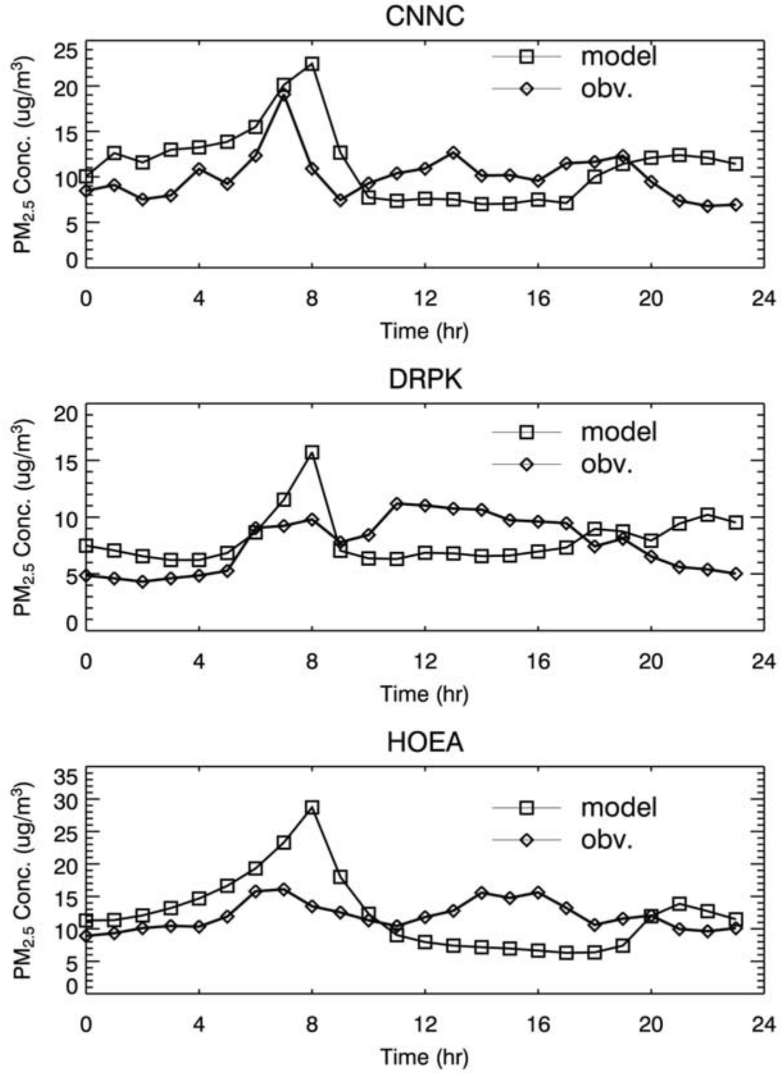

Figure 7. Site-by-site comparisons of the simulated and measured hourly PM$_{2.5}$ mass concentrations. The simulated and measured values are averaged over the time period when the observations are available.

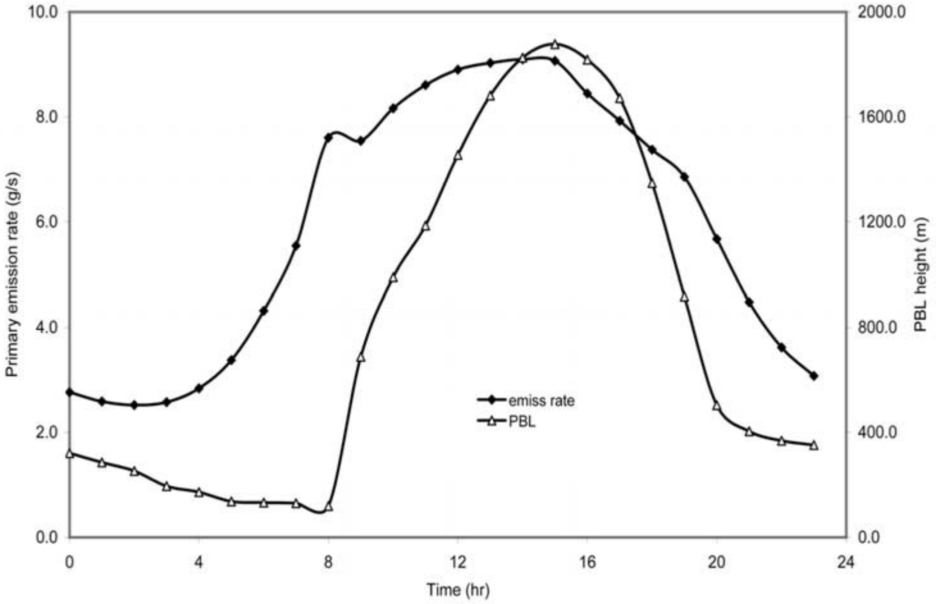

Figure 8. Diurnal variations of the primary emitted $PM_{2.5}$ and PBL height averaged over the monitoring sites and the episode.

very high because of automobile emissions. The calculated PBL height also reached the lowest value around sunrise. Hence the simulated strong morning peak is apparently associated with the PBL height.

[18] The ratio of organic carbon to elemental carbon is often used to distinguish the relative importance of primary and secondary organics. If the predicted ratios of OC/EC are higher than those assumed to occur from primary emissions (a ratio between 2 and 5 is generally assumed for OC/EC from primary emissions [*Strader et al.*, 1999], the excess OC is assumed to be due to secondary organic aerosol (SOA) formation. Figure 9 shows the scatterplots of OC/EC ratios in the study domain on 26 and 27 August. About 42% of the OC/EC ratios are above 5.0, suggesting that most of the OC is not due to the secondary organic aerosol (SOA) formation in our simulations. Since the measurements indicate that much of organic carbon is from SOA formation in this region [*Allen*, 2002; *Russell et al.*, 2004], the modeled SOA formation is likely underpredicted.

[19] Figure 10 shows the temporal variations of organic carbon, sulfate and SOA averaged over the monitoring sites and the simulation days. The formation of the secondary fine particulate matter such as sulfate and SOA reaches the highest in the morning because of strong emissions, low calculated PBL heights, and rapid photochemical activity after sunrise, contributing to the strong morning peak. Most of organic carbon arises from the primary sources. The SOA formation is rather low, with the highest value of about 1.7 $\mu g/m^3$. SOA accounts for about 28% of the organic carbon. Field measurements, however, imply that SOA accounts mainly for the organic carbon mass [*Allen*, 2002; *Russell et al.*, 2004]. The model simulations suggest that

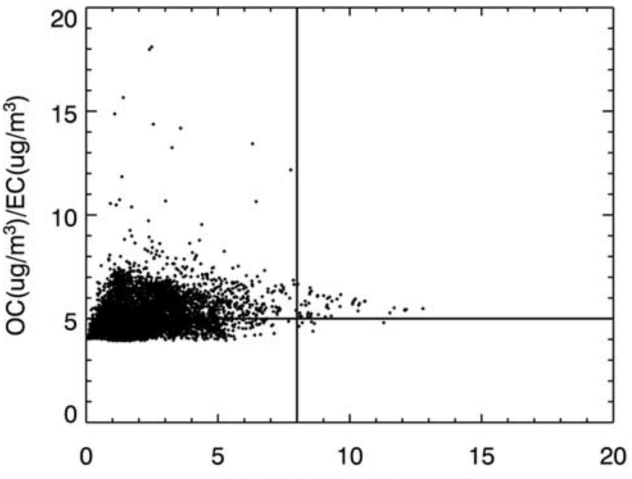

Figure 9. Scatterplot of the ratio of OC/EC versus organic carbon over the study domain on 26 and 27 August 2000.

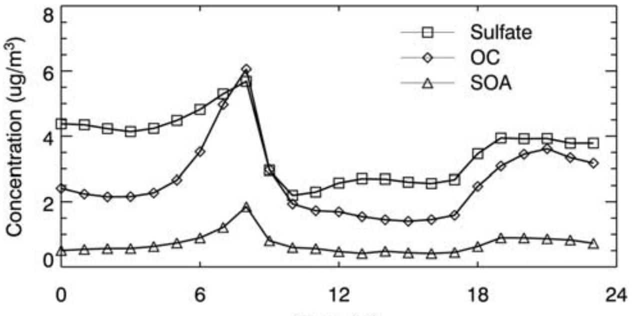

Figure 10. Diurnal variations of the major constituents of $PM_{2.5}$ averaged over the monitoring sites and the episode.

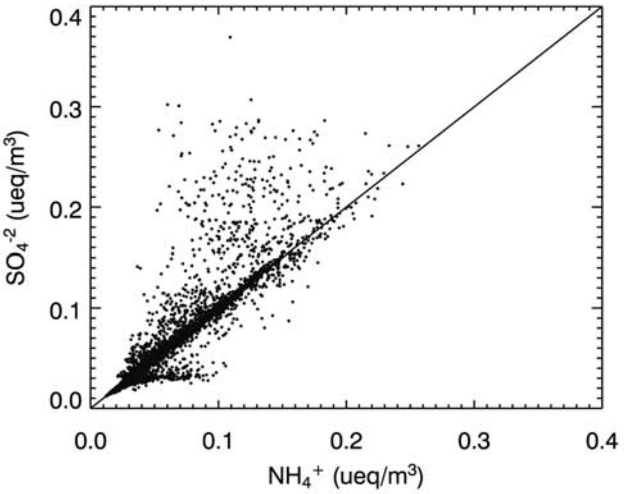

Figure 11. Scatterplot of sulfate versus ammonium in equivalents over the study domain on 26 and 27 August 2000.

about 40% of SOA is formed from anthropogenic precursors and 60% is formed from biogenic precursors. The underprediction in SOA is likely caused by underprediction of the emissions of anthropogenic SOA precursors. A recent measurement [*Karl et al.*, 2003] shows that the emissions of aromatic compounds such as benzene and toluene are dramatically underestimated in the previous emission inventories in Houston. It is likely that the increase in the emission inventory for SOA precursors in our simulations may still be inadequate. Also, the SOA formation chemistry especially related to aqueous reactions within the CMAQ aerosol module might be inadequate, since the SOA production was not very sensitive to the increase of the SOA precursor emissions.

[20] The overall acidity of the fine particulate matter can be assessed through a cation-anion balance, based on the chemical composition data. Since the nitrate mass is low and sulfuric acid is the primary source of the acidity in Houston, the majority of the ammonium is expected to neutralize sulfate to form ammonium sulfate ($(NH_4)_2SO_4$) or ammonium bisulfate (NH_4HSO_4). The scatterplot of sulfate concentrations to ammonium concentrations in equivalents from the model predictions for the study domain on August 26 and 27 is shown in Figure 11 (assuming all sulfate is represented as SO_4^{2-}). About 55% of the points fall above the 1:1 line, indicating that the ammonium is entirely taken up in neutralizing sulfate. Since the major species responsible for neutralizing acidity is ammonia, the fine particle matter in this region is slightly acidic. It is likely that sodium from the sea salt (coarse particles) in this region may also neutralize some of the excess sulfate as another important additional cation [*Allen*, 2002; *Russell et al.*, 2004].

[21] The fine particulate matter is formed from the primary sources, i.e., direct emissions, and secondary sources, which are formed in the atmosphere through chemical transformations. Field measurements indicate that the secondary fine particulate matter accounts for 50–60% of the $PM_{2.5}$ mass at urban sites in Houston [*Allen*, 2002]. Our simulated values are about 50%, consistent with the field measurements.

4. Conclusion

[22] This work investigates fine particulate matter and its major components during an eight-day episode (24 to 31 August 2000) in Houston by model simulations. The results are evaluated for model performance by comparing with the field measurements during the episode. Generally, the predicted daily mass concentrations of $PM_{2.5}$ and its major components are in good agreement with the observations. The predicted daily $PM_{2.5}$ mass concentrations are about 8.5–13.0 $\mu g/m^3$, comparable to the measured values, 8.0–14.0 $\mu g/m^{3.}$ The diurnal patterns of $PM_{2.5}$ mass concentrations are consistent nearly throughout the region, with a strong morning peak and a weaker peak in the late afternoon to the early evening. High primary emissions, high formation rates of the secondary fine particulate matter such as sulfate and SOA, and low PBL heights contribute to the morning peak. The geographical distribution indicates that the $PM_{2.5}$ mass concentration is rather spatially homogeneous throughout the Houston area. The major components of the fine particulate matter in the area are sulfate, organic carbon, elemental carbon and ammonium. Their predicted contents are about 30%, 27%, 5%, and 10% of total $PM_{2.5}$ mass, respectively. The balance of the primary cations and anions indicates that fine particulate matter in this region is acidic. The model yields good simulations of the averaged daily mass concentrations of the major components such as sulfate, organic carbon, elemental carbon and ammonium with the NMBs less than ±25%. However, the model underpredicts nitrate with the NMB value of about 61%. Uncertainties in the aerosol precursor emissions, the aerosol chemistry especially about SOA formation and aqueous reactions, and the PBL heights are likely responsible for the differences.

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