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Comparative evaluation of the impact of WRF/NMM and WRF/ARW meteorology on CMAQ simulations for $PM_{2.5}$ and its related precursors during the 2006 TexAQS/GoMACCS study

S. Yu, R. Mathur, J. Pleim, G. Pouliot, D. Wong, B. Eder, K. Schere, R. Gilliam, and S. T. Rao

Atmospheric Modeling and Analysis Division, National Exposure Research Laboratory, US Environmental Protection Agency, Research Triangle Park, NC 27711, USA

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Correspondence to: S. Yu (yu.shaocai@epa.gov)

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Abstract

This study presents a comparative evaluation of the impact of WRF-NMM and WRF-ARW meteorology on CMAQ simulations of $PM_{2.5}$, its composition and related precursors over the eastern United States with the intensive observations obtained by aircraft (NOAA P-3), ship and surface monitoring networks (AIRNow, IMPROVE, CASTNet and STN) during the 2006 TexAQS/GoMACCS study. The results at the AIRNow surface sites show that both ARW-CMAQ and NMM-CMAQ reproduced day-to-day variations of observed $PM_{2.5}$ and captured the majority of observed $PM_{2.5}$ within a factor of 2 with a NMB value of −0.4 % for ARW-CMAQ and −18 % for NMM-CMAQ. Both models performed much better at the urban sites than at the rural sites, with greater underpredictions at the rural sites. Both models consistently underestimated the observed $PM_{2.5}$ at the rural IMPROVE sites by −1 % for the ARW-CMAQ and −19 % for the NMM-CMAQ. The greater underestimations of SO_4^{2-}, OC and EC by the NMM-CMAQ contributed to increased underestimation of $PM_{2.5}$ at the IMPROVE sites. The NMB values for $PM_{2.5}$ at the STN urban sites are 15 % and −16 % for the ARW-CMAQ and NMM-CMAQ, respectively. The underestimation of $PM_{2.5}$ at the STN sites by the NMM-CMAQ mainly results from the underestimations of the SO_4^{2-}, NH_4^+ and TCM components, whereas the overestimation of $PM_{2.5}$ at the STN sites by the ARW-CMAQ results from the overestimations of SO_4^{2-}, NO_3^-, and NH_4^+. The comparison with P-3 aircraft measurements reveals that both ARW-CMAQ and NMM-CMAQ have very similar model performance for vertical profiles for $PM_{2.5}$ chemical components (SO_4^{2-}, NH_4^+) and related gaseous species (HNO_3, SO_2, NH_3, isoprene, toluene, terpenes) as both models used the same chemical mechanisms and emissions. The results of ship along the coast of southeastern Texas over the Gulf of Mexico show that both models captured the temporal variations and broad synoptic change seen in the observed HCHO and acetaldehyde with the means NMB < 30 % most of the time but they consistently underestimated terpenes, isoprene, toluene and SO_2.

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1 Introduction

Fine particulate matter ($PM_{2.5}$, particles with aerodynamic diameters less than 2.5 µm) results from primary direct emissions and secondary formation through atmospheric oxidation of gaseous precursors such as sulfur oxides (SO_x), nitrogen oxides (NO_x) and volatile organic compounds (VOCs), and subsequent gas-to-particle conversion processes. To reflect more recent health effect studies and provide increased protection of public health and welfare, the level of the 24-h $PM_{2.5}$ National Ambient Air Quality Standards (NAAQS) has been revised from 65 µg m^{-3} to 35 µg m^{-3}, effective on 18 December 2006 (Federal Register, 2006). The rationale for this revision includes consideration of: (1) evidence of health effects related to short- and long-term exposures to fine particles; (2) insights gained from a quantitative risk assessment; and (3) specific conclusions regarding the need for revisions to the current standards and the elements of $PM_{2.5}$ standards (i.e., indicator, averaging time, form, and level) that, taken together, are requisite to protect public health with an adequate margin of safety (Federal Register, 2006). Unlike O_3 pollution which occurs typically during the high pressure, hot, sunny and stagnant atmospheric conditions at the locations with substantial VOC and NO_x concentrations, elevated $PM_{2.5}$ concentrations occur throughout the year because $PM_{2.5}$ is composed of a variety of particles differing in size and chemical composition and also because source emissions of each component of the atmospheric particles vary differently and seasonally.

The relationship between $PM_{2.5}$ and meteorological conditions has been examined by several studies (Whiteaker et al., 2002; Wehner and Wiedensohler, 2003; Wise and Comrie, 2005; Dawson et al., 2007). The meteorological conditions can have complex effects on the concentrations of $PM_{2.5}$ due to the fact that $PM_{2.5}$ is comprised of many different species and the meteorological impacts on individual species are different. For example, in the study of sensitivity of $PM_{2.5}$ to various meteorological parameters in the eastern US, Dawson et al. (2007) showed that the strongest effects of changes in meteorology on $PM_{2.5}$ concentrations were from temperature, wind speed,

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absolute humidity, mixing height and precipitation effects, whereas cloud liquid water content, optical depth and cloudy area can lead to small changes in $PM_{2.5}$ on average with appreciable responses in some areas. The changes in concentrations of $PM_{2.5}$ caused by changes in meteorology should be taken into account in long-term air quality management as concluded by them.

The 2006 Texas Air Quality Study/Gulf of Mexico Atmospheric Composition and Climate Study (TexAQS/GoMACCS) was a joint regional air quality and climate change study conducted during the late summer (1 August to 15 October 2006). The objective of the program is to provide a better understanding of the sources and atmospheric processes responsible for the formation and distribution of ozone and aerosols in the atmosphere, their impact on human health and regional haze as well as the influence on the radiative forcing of climate over Texas and the northwestern Gulf of Mexico. The comprehensive observational data from the 2006 TexAQS/GoMACCS can be used to examine in detail the performance of air quality models from a multipollutant perspective, in terms of their surface concentrations as well as vertical distributions. In this study, we examine the impact of these two different meteorological fields (WRF-ARW and WRF-NMM) on the CMAQ simulations for $PM_{2.5}$, its chemical composition and precursors. The purpose of this paper is twofold. First, this study comparatively examines the impact of these two different meteorological fields on CMAQ simulations for vertical profiles of $PM_{2.5}$, its chemical composition and precursors on the basis of the extensive measurements obtained by aircraft and ship during the 2006 TexAQS/GoMACCS field experiment, especially, for three types of plumes (power plant plumes, Houston and Dallas urban plumes and Ship Channel plumes) over the Houston-Galveston-Brazoria (HGB) and Dallas-Fort Worth (DFW) metropolitan areas. Second, the influence of these two different meteorological fields on spatial and temporal variations of $PM_{2.5}$, and its chemical composition over the eastern US is evaluated against the observations from the surface monitoring networks (AIRNOW, IMPROVE, CASTNet and STN) during the 2006 TexAQS/GoMACCS study.

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2 Description of the modeling system and observational databases

2.1 Description of the modeling system

The detailed description of the modeling system and configurations is given by Yu et al. (2011). Here a brief summary relevant to the present study is presented. The WRF model is a new state-of-science mesoscale model framework with two available dynamic cores: the Non-hydrostatic Mesoscale Model (NMM) developed by NCEP (Janjic, 2003) and the Advanced Research WRF (ARW) developed by NCAR (Skamarock et al., 2005). The NMM core uses a terrain-following hybrid (sigma-pressure) vertical coordinate and Arakawa E-grid staggering for horizontal grid, whereas the ARW core uses a terrain-following hydrostatic-pressure vertical coordinate with vertical grid stretching permitted and Arakawa C-grid staggering for horizontal grid. In this study, both WRF-ARW and WRF-NMM are employed to provide meteorological fields for CMAQ (the notations ARW-CMAQ and NMM-CMAQ will be used hereafter to represent these two configurations). The Carbon Bond chemical mechanism (version 4.2) has been used to represent photochemical reaction pathways in both NMM-CMAQ and ARW-CMAQ.

The area source emissions are based on the 2001 National Emission Inventory (NEI). The point source emissions are based on the 2001 CEM estimates of SO_2 and NO_x projected to 2006 on a regional basis using the Department of Energy's 2006 Annual Energy Outlook issued in January of 2006. The mobile source emissions were generated by EPA'S MOBILE6 model using 1999 Vehicle Miles Traveled (VMT) data and a fleet year of 2006. For the NMM-CMAQ run, the results from the target forecast period (04:00 UTC to next day's 03:00 UTC) based on the 12:00 UTC NMM-CMAQ simulation cycle over the domain of the continental United States (see Fig. 1a of Yu et al., 2011) are used, whereas the ARW-CMAQ model was applied over a domain encompassing the eastern United States (see Fig. 1b of Yu et al., 2011) and was run continuously over the whole period.

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The aerosol module in CMAQ is described by Binkowski and Roselle (2003) and updates are described by Bhave et al. (2004) and Yu et al. (2007). The size distribution of aerosols in tropospheric air quality models can be represented by the sectional approach (Zhang et al., 2004), the moment approach (Yu et al., 2003), and the modal approach (Binkowski and Roselle, 2003). In the aerosol module of the CMAQ, the aerosol distribution is modeled as a superposition of three lognormal modes that correspond nominally to the ultrafine (diameter (D_p) < 0.1 mm), fine (0.1 < D_p < 2.5 mm), and coarse (D_p > 2.5 mm) particle size ranges. Each lognormal mode is characterized by total number concentration, geometric mean diameter and geometric standard deviation. The model results for $PM_{2.5}$ concentrations are obtained by summing aerosol species concentrations over the first two modes. Generally speaking, the modal approach offers the advantage of being computationally efficient, whereas the sectional representation provides more accuracy at the expense of computational cost. The CMAQ model is able to simulate the integral properties of fine particles such as $PM_{2.5}$ mass and visible aerosol optical depth reasonably well but it cannot resolve PM size distributions accurately (Yu et al., 2008). In this study, we only present the model performance for $PM_{2.5}$ mass but not size distributions.

2.2 Observational databases

Four surface monitoring networks for $PM_{2.5}$ measurements were employed in this evaluation (Interagency Monitoring of Protected Visual Environments (IMPROVE), Speciated Trends Network (STN), Clean Air Status Trends Network (CASTNet) and Air Quality System (AQS)), each with its own and often disparate sampling protocol and standard operating procedures. In the IMPROVE network, two 24-h samples are collected on quartz filters each week, on Wednesday and Saturday, beginning at midnight local time (Sisler and Malm, 2000). The observed $PM_{2.5}$, SO_4^{2-}, NO_3^-, EC and OC data are available at 71 rural sites across the eastern United States. The STN network (http://www.epa.gov/air/data/aqsdb.html) follows the protocol of the IMPROVE network (i.e., every third day collection) with the exception that most of the sites are in urban

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areas. The observed $PM_{2.5}$, SO_4^{2-}, NO_3^-, and NH_4^+ data are available at 178 STN sites within the model domain. The CASTNet (http://www.epa.gov/castnet/) collected the concentration data at predominately rural sites using filter packs that are exposed for 1-week intervals (i.e., Tuesday to Tuesday). The aerosol species at the 34 CASTNet sites used in this evaluation include: SO_4^{2-}, NO_3^-, and NH_4^+. The hourly near real-time $PM_{2.5}$ data at 309 sites in the eastern United States are measured by tapered element oscillating microbalance (TEOM) instruments at the US EPA's Air Quality System (AQS) network sites. In addition, measurements of vertical profiles of $PM_{2.5}$, its related chemical composition and gas species (CO, NO, NO_2, HNO_3, PAN, ethylene), and meteorological parameters (liquid water content, water vapor, temperature, wind speed and direction, and pressure) were carried out by instrumented aircraft (NOAA P-3) and a research ship deployed as part of the 2006 TexAQS/GoMACCS field experiment. The detailed instrumentation and protocols for measurements are described at http://esrl.noaa.gov/csd/2006/fieldops/mobileplatforms.html. The flight tracks of the P-3 aircraft, and ship movements are presented in Fig. 2 of the Part 1 paper. The results for comparison of the impact of two meteorological models on CMAQ simulations over the eastern US (e.g., ARW domain as shown in Fig. 1b of the Part 1 paper) during the period of 6 August and 6 October 2006 are presented in this study.

3 Results and discussions

3.1 Impact of meteorology on spatial and temporal variations of $PM_{2.5}$ over the eastern US domain at the AQS sites

Table 1 summarizes the comparison results of the ARW-CMAQ and NMM-CMAQ for the daily (24-h) average $PM_{2.5}$ concentrations. Following the protocol of the IMPROVE network, the daily (24-h) $PM_{2.5}$ concentrations at the AQS sites were calculated from midnight to midnight local time of the next day on the basis of hourly $PM_{2.5}$ observations. The evaluation results at the urban and rural sites are also summarized in

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Table 1. The domain wide mean values of mean bias (MB) and root mean square error (RMSE) (Yu et al., 2006) for all daily $PM_{2.5}$ at the AQS sites during the 2006 TexAQS/GoMACCS period are −0.1 (−2.3) and 7.9 (7.6) $\mu g\,m^{-3}$ for ARW-CMAQ (NMM-CMAQ), respectively, and those for normalized mean bias (NMB) and normalized mean error (NME) are −0.4 (−18.4) % and 43.7 (44.3) % for ARW-CMAQ (NMM-CMAQ), respectively. It is of interest to note that both models performed much better at the urban sites than at the rural sites, with greater underpredictions at the rural sites. As shown in Sect. 3.2, the underestimation of $PM_{2.5}$ at the STN urban sites by the NMM-CMAQ mainly results from the underestimations of the SO_4^{2-}, NH_4^+ and TCM components, whereas the overestimation of $PM_{2.5}$ at the STN sites by the ARW-CMAQ results from the overestimations of SO_4^{2-}, NO_3^-, NH_4^+, and OTHER. The greater underestimations of SO_4^{2-}, OC and EC by the NMM-CMAQ led to more underestimation of $PM_{2.5}$ at the IMPROVE rural sites. Since TEOM measurements for $PM_{2.5}$ at the AQS sites should be considered as lower limits because of volatilization of soluble organic carbon species in the drying stages of the measurement (Grover et al., 2005), the underprediction by the model is likely more severe than this evaluation suggests.

Additional insight into the negative bias (underestimation) and errors (scatter) of both models can be gained from Fig. 1a for the scatter plot and Fig. 1b for the NMB values as a function of the different observed $PM_{2.5}$ concentration ranges. Table 1 and Fig. 1 depict that the model performance for ARW-CMAQ and NMM-CMAQ is similar and reasonable for the $PM_{2.5}$ concentration with very close values of RMSE, NME, and correlation coefficient for both models although the ARW-CMAQ has the slightly better performance on the basis of values of MB and NMB. Figure 1a and b clearly indicate that both ARW-CMAQ and NMM-CMAQ models reproduced the majority of the observed daily $PM_{2.5}$ concentrations within a factor of 2, especially for the concentration range of 10 to 35 $\mu g\,m^{-3}$. However, both models overestimated the observations in the low $PM_{2.5}$ concentration range (<10 $\mu g\,m^{-3}$) with NMB values of 37.8 % (ARW-CMAQ) and 15.6 % (NMM-CMAQ), respectively, but underestimates the observations in the high $PM_{2.5}$ concentration range (>10 $\mu g\,m^{-3}$) consistently. The small NMB value (−0.4 %)

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for the ARW-CMAQ model results from the compensation error between large $PM_{2.5}$ overestimation for low $PM_{2.5}$ concentration portion ($<10\,\mu g\,m^{-3}$) and underestimation of high $PM_{2.5}$ concentration portion ($>10\,\mu g\,m^{-3}$) as indicated in Fig. 1b. The spatial distributions of NMB values for ARW-CMAQ (Fig. 1c) and NMM-CMAQ (Fig. 1d) show that both models had large underestimation of the observed daily $PM_{2.5}$ concentrations in the southeast, especially for the NMM-CMAQ. To investigate the model performance over time, the values of mean, MB, RMSE, NMB, NME and correlation coefficient (r) were calculated (domain wide averages) and plotted as daily time series for the daily $PM_{2.5}$ concentrations as shown in Fig. 2. The NMB values range from −50.4 % (23 September) to 18.9 % (25 September) for NMM-CMAQ and from −36.8 % (7 August) to 41.1 % (2 October) for the ARW-CMAQ. Both models had slightly consistent underestimations of $PM_{2.5}$ for the first period from 6 August to 3 September but general overestimations after 3 September. The domain daily mean $PM_{2.5}$ concentrations for the ARW-CMAQ are consistently about 17 % higher than those for the NNM-CMAQ during the 2006 TexAQS/GoMACCS period although the RMSE, NME and correlation coefficient values are close for these two models as shown in Fig. 2.

3.2 Influence of meteorology on spatial and temporal evaluation for $PM_{2.5}$ and its chemical components at the CASTNet, IMPROVE, STNsites over the eastern US

The scatter plots of Fig. 3a indicate that at the IMPROVE, CASTNet and STN sites, both ARW-CMAQ and NMM-CMAQ captured a majority of observed SO_4^{2-}, NH_4^+, $PM_{2.5}$ concentrations within a factor of 2. The examination of the domain-wide bias and errors (Table 2) for different networks reveals that the NMM-CMAQ consistently underestimated the observed mean SO_4^{2-} by 29 %, 18 % and 14 % at the CASTNet, IMPROVE and STN sites, respectively, whereas the ARW-CMAQ overestimated the observed mean SO_4^{2-} by 16 % and 27 % at the IMPROVE and STN sites, respectively, with slight underestimation of 10 % at the CASTNet site. Both models overestimated the observed NH_4^+ at the STN sites (by 45 % for ARW-CMAQ and 33 % for NMM-CMAQ) but

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underestimated at the CASTNet sites (by −3 % for ARW-CMAQ and −22 % for NMM-CMAQ). Both models overestimated the observed SO_2 by more than 80 % at the CASTNet sites. The comparison of the modeled and observed total sulfur ($SO_4^{2-} + SO_2$) at the CASTNet sites in Fig. 3b reveals that both models overestimated the observed total sulfur symmetrically and the modeled mean total sulfur values are higher than the observations by 37 % and 21 % for ARW-CMAQ and NMM-CMAQ, respectively. This indicates too much SO_2 emission in the emission inventory.

The poor model performance for NO_3^- (see scatter plot in Fig. 3a and correlation <0.40 except that at the STN sites for the NMM-CMAQ in Table 2) is related in part to volatility issues of measurements associated with NO_3^-, and their exacerbation because of uncertainties associated with SO_4^{2-} and total NH_4^+ simulations in the model (Yu et al., 2005). Table 2 indicates that both models underestimated the observed mean OC, EC and TC concentrations at the IMPROVE sites by −11 %, −12 % and −11 % for the ARW-CMAQ, respectively, and by −20 %, −28 % and −21 % for the NMM-CMAQ, respectively. Note that since the STN network used the thermo-optical transmittance (TOT) method to define the split between OC and EC while the IMPROVE and the model emission inventory use the thermo-optical reflectance (TOR) method, only the determination of total carbon (TC = OC + EC) is comparable between these two analysis protocols (Yu et al., 2004). Therefore, Table 2 only lists the performance results for TC comparisons from the STN sites. Both models consistently underestimated the observed TC concentrations at the STN sites by −25 % for ARW-CMAQ and −42 % for NMM-CMAQ. As pointed out by Yu et al. (2007), factors contributing to this underestimation of the modeled OC include: (1) missing sources of primary OC in emission inventory used for the summer, (2) underestimation of secondary OC (SOA) formation such as sources from the oxidation of isoprene and sesquiterpenes (Edney et al., 2005) and an aqueous-phase mechanism for SOA formation from the oxidation of VOCs (Carlton et al., 2006) that were not yet included in the version of the CMAQ model used here. Morris et al. (2006) found that including the SOA formation from sesquiterpene and isoprene improved the CMAQ model performance for OC.

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Figure 4 shows comparisons of stacked bar-plots for observed and modeled concentrations for each chemical constituent of $PM_{2.5}$ at the STN sites. Note that "OTHER" species in Fig. 4 refers to unspecified anthropogenic mass which comes from the emission inventory of $PM_{2.5}$, i.e., $[PM_{2.5}] = [SO_4^{2-}] + [NH_4^+] + [NO_3^-] + [TCM] + [OTHER]$. Since organic compounds comprising ambient particulate organic mass are largely unknown, an average multiplier is frequently used to convert measurements of OC (typically reported as $\mu g\,C\,m^{-3}$) to organic carbonaceous aerosol mass (OCM). The value of 1.4 has been widely used to estimate particulate organic mass (e.g., Turpin and Lim, 2001) from measured OC and is also used in our analysis. The ARW-CMAQ overestimated the observed $PM_{2.5}$ at the STN sites (most of them are located in urban areas) by 15 %, whereas the NMM-CMAQ underestimated by −16 % as listed in Table 2. The stacked bar-plots of Fig. 4 show that the underestimation of $PM_{2.5}$ at the STN sites by the NMM-CMAQ mainly results from the underestimations of the SO_4^{2-}, NH_4^+ and TCM components, whereas the overestimation of $PM_{2.5}$ at the STN sites by the ARW-CMAQ results from the overestimations of SO_4^{2-}, NO_3^-, NH_4^+, and OTHER although the ARW-CMAQ still underestimated the observed TCM. On the other hand, both models consistently underestimated the observed $PM_{2.5}$ at the IMPROVE sites (most of them are located in rural areas) by −1 % for the ARW-CMAQ and −19 % for the NMM-CMAQ. The notable underestimations of SO_4^{2-}, OC and EC by the NMM-CMAQ led to the underestimation of $PM_{2.5}$ at the IMPROVE sites as shown in Table 2. These results suggest a need to improve accuracy of TCM at both rural and urban sites. On the basis of analysis of the diurnal cycles from the AQS $PM_{2.5}$ monitors and comparison with model median diurnal cycles over the northeastern US during the 2004 ICARTT study, McKeen et al. (2007) found some inconsistencies with certain processes within the models and the observations. They found very little diurnal variation in the median observed diurnal cycles at urban and suburban monitor locations. However, significant diurnal variability was exhibited by some models, such as the Eta-CMAQ, that does not capture the decrease of observed $PM_{2.5}$ from 01:00 to 06:00 LT, indicating a reduced role for aerosol loss during the late night and early morning hours

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(McKeen et al., 2007). The large scatter in Fig. 2 for $PM_{2.5}$ can also arise due to inadequate representation of the diurnal evolution of observed $PM_{2.5}$ by both ARW-CMAQ and NMM-CMAQ.

3.3 Influence of meteorology on vertical profiles for $PM_{2.5}$ chemical components (SO_4^{2-}, NH_4^+), and its related gas species from 2006 TexAQS/GoMACCS

The same approach used in the Part 1 paper was used to extract model (ARW-CMAQ, NMM-CMAQ) results for comparison with the aircraft P-3 measurements. The observed and modeled data pairs were grouped according to the model layer for each day and each flight. The vertical profiles from both models and observations obtained in this manner can be regarded to represent average conditions encountered over the study domain. We refer to these average regional vertical variations as composite vertical distributions in the subsequent discussions. Table 3 summarizes the specific missions and weather conditions encountered for each flight used in this study. P-3 conducted most of its measurements during the daytime (~09:40 to ~17:00 LST) except on 29 September when the P-3 measurements were conducted into night (13:45 to 20:10 LST). As summarized by McKeen et al. (2009), the P-3 spent a significant fraction of its allocated flight time between 300 and 700 m above the ground and had 10 daytime flights between 13 and 29 September 2006 which consisted of upwind and downwind transects of the Houston and Dallas urban areas. Figure 5 presents modeled and observed daily composite vertical distributions for $PM_{2.5}$ chemical components (SO_4^{2-}, NH_4^+) and related gaseous species (HNO_3, SO_2, NH_3, VOC (isoprene, toluene, terpene)) during the 2006 TexAQS/GoMACCS period. Mean composite vertical distributions according to the model layer for the models (ARW-CMAQ and NMM-CMAQ) and observations for the whole period are summarized in Table 4.

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3.3.1 Vertical profiles of SO_4^{2-}, and NH_4^+

As shown in Fig. 5 and Table 4, both ARW-CMAQ and NMM-CMAQ generally estimated SO_4^{2-} reasonably well on most days except on 9/16 and 9/21 in which the NMM-CMAQ had consistently high SO_4^{2-}. NMM-CMAQ also has consistently high NH_4^+ on 9/16 and 9/21 relative to both observation and ARW-CMAQ. As analyzed in McKeen et al. (2009), on both 9/15 and 9/21, the air masses originating from western Louisiana merging with the Houston plume with high CO, organic aerosol and EC but relative reduced enhancements of NO_y, SO_2 and toluene were sampled by the P-3. There was an additional influence of an aged continental air mass from the east or southeast affecting the northeastern Houston with a possible biomass burning signature (McKeen et al., 2009). These characteristics of air masses may make some contribution to the poor performance of NMM-CMAQ for SO_4^{2-} and NH_4^+ on 9/21. Figure 5 and Table 4 reveal that both models often overestimated NH_4^+ vertically except at layer 1, whereas both models systematically underestimated the NH_3 vertically for all altitudes. The large systematical underestimations of NH_3, in part, result from the general overestimations of NH_4^+ because too much of TNH_4 (e.g., $NH_4^+ + NH_3$) were put into the aerosol phase by the ISORROPIA thermodynamic model and the model results at low NH_3 concentrations were very sensitive to any errors in SO_4^{2-} and TNH_4 in the simulations (Yu et al., 2005). On the other hand, both models performed reasonably well for observed SO_4^{2-} and NH_4^+ on 9/13 and 9/25 over the Dallas-Fort Worth (DFW) region although their concentrations were generally lower than those over the Houston urban and industrial areas as shown in Fig. 5. The P-3 flights sampled the plumes downwind of refining and petrochemical regions outside of Houston, Beaumont-Port Arthur, and the Houston Ship Channel region on 9/15, 9/20 and 9/27, respectively. Both models captured the observed SO_4^{2-} and NH_4^+ in these downwind plumes well as shown in Fig. 5. Table 4 also shows that the mean SO_4^{2-} concentration (2.35 $\mu g\, m^{-3}$) of ARW-CMAQ is slightly higher than that of NMM-CMAQ (2.24 $\mu g\, m^{-3}$) although the mean NH_4^+ concentrations are very close for the two models.

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3.3.2 Vertical profiles for NH_3, SO_2 and HNO_3

Figure 5 shows the comparison of the modeled and observed daily composite vertical distributions for NH_3, SO_2 and HNO_3. As summarized in Table 4 and Fig. 5, both models consistently underestimated NH_3 on most days except on 9/25. The mean NH_3 concentrations of observations, ARW-CMAQ and NMM-CMAQ are 1.05, 0.41 and 0.37 ppbv, respectively (see Table 4). As indicated previously, the ISORROPIA thermodynamic model put too much of TNH_4 (e.g., $NH_4^+ + NH_3$) into the aerosol phase, leading to the systematical underestimations of NH3. The reasonable performance for all aerosol related species (NH_3, HNO_3, NH_4^+ and SO_4^{2-}) on 9/25 seems to cause the reasonable partitioning of TNH_4 between gaseous and aerosol phases. Both models generally estimated HNO_3 reasonably well on most days except on 9/15, 9/29 and 10/6 in which both models had consistently high HNO_3 as indicated in Fig. 5. The mean observed and modeled SO_2 concentrations are close with general overestimations near ground and general underestimations at high altitudes as indicated in Table 4. The relative reduced enhancements of SO_2 on 9/15 and 9/21 is because the air masses originating from western Louisiana were merged with the Houston plums and influenced by an aged continental air mass from the east or southeast for these two days. Both models seem to capture the observed SO_2 on these days well as shown in Fig. 5.

3.3.3 Vertical profiles for terpenes, toluene, and isoprene

As analyzed by Ying and Krishnan (2010), biogenic emissions are the largest contributor to the VOC emissions and are almost an order of magnitude higher than all other sources combined over the southeastern Texas domain. The main anthropogenic VOC sources are from petroleum and other industrial sources, and highway gasoline vehicles. Biogenic monoterpenes and isoprene emission rates are high over the coniferous forests of North America, especially in the summer months (Guenther et al., 2000), providing gas precursors for the formation of biogenic secondary organic aerosols (SOA). Anthropogenic toluene stems predominantly from automotive emissions. In the CMAQ

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aerosol module, biogenic and anthropogenic SOA occur exclusively by absorptive partitioning of condensable oxidation products of aromatic (mainly toluene) and monoterpene compounds into a pre-existing organic-aerosol phase (Yu et al., 2007).

The model's ability to simulate the composite vertical distributions for isoprene, terpene and toluene, as measured by the P-3, is illustrated in Fig. 5 and summarized in Table 4. Both ARW-CMAQ and NMM-CMAQ have the similar performances for these VOC species. In general, both models captured the vertical variation patterns of the observed isoprene quite well on most days, except on 9/13 and 9/15. The summaries in Table 4 indicate that both models have reasonable performance for isoprene at the low altitudes (<2000 m) but completely missed the observed isoprene at the high altitudes (>2000 m). A noticeable discrepancy is the consistent underestimation of terpenes by a factor of 2 to 4 by both models (the mean ARW-CMAQ, NMM-CMAQ and observed terpene concentrations for all data are 10.2, 9.7 and 32.1 ppt, respectively) vertically from the low to high altitudes on most days as shown in Fig. 5 and Table 4, especially at the high altitudes (>~1500 m). On the other hand, both models captured the observed toluene well (the mean ARW-CMAQ, NMM-CMAQ and observed toluene concentrations for all data are 118.0, 113.9 and 127.2 ppt, respectively, see Table 4) although both models had slight overestimation near the ground and underestimation at the high altitudes (>~2000 m). The emission inventory for biogenic emissions of isoprene and monoterpenes is highly uncertain, possibly explaining the general underestimations of isoprene and monoterpenes. Since the underestimations of terpenes will cause underestimation of biogenic SOA, leading to the underestimation of OC, improvement of the VOC emission inventory is recommended in order to provide better model results for these species.

3.4 Influence of meteorology on the time-series over the Gulf of Mexico with the *Ronald H. Brown* ship observations

The time-series comparisons of the observations and models (ARW-CMAQ and NMM-CMAQ) for $PM_{2.5}$ precursors (NH_3, SO_2, toluene, isoprene, terpenes, HCHO and

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acetaldehyde) along the ship tracks (see Fig. 2 of Part 1) during the 2006 TexAQS/GoMACCS period are shown in Fig. 6 and summarized in Table 5. As mentioned in Part 1, most of ship's time was spent sampling along the coast of southeastern Texas over the Gulf of Mexico from 5 August to 11 September 2006. Both models have similar performance for each species as indicated in Table 5. Both models captured the temporal variations and broad synoptic change seen in the observed HCHO and acetaldehyde with the means NMB < 30 % along the ship track most of the time although with some occasional major excursions (see Fig. 6). Like those on the basis of P-3 observations (see Sect. 3.3), both models underestimated biogenic VOCs, such as terpenes, by more than a factor of 2 and isoprene by more than 30 %. On the other hand, both models also underestimated SO_2 and toluene which are mainly from anthropogenic sources. Both models also missed most of the peak NH_3 concentrations although the means of both models are close to the observations as shown in Table 5 and Fig. 6. The rapid increases of observed NH_3, SO_2, toluene, HCHO and acetaldehyde on 2 September are because the ship was anchored in the Barbour's Cut inlet located off Galveston Bay near Houston Ship Channel. Both models missed most of high concentrations for these species. As analyzed in the Part 1, the complexity over the coastal region of the Gulf of Mexico with highly variable mixing depth in space and time because of land-sea contrast, the sea-breeze cycle, land-use differences and along-shore coastal irregularities causes both models to be unable to simulate the transport well over land-ocean interface.

4 Conclusions

A detailed evaluation of the impact of WRF-ARW and WRF-NMM meteorology on CMAQ simulations for $PM_{2.5}$, its chemical components and its related precursors has been carried out over the eastern US by comparing the model results with the observations from a variety of surface monitoring networks and aircraft obtained during the 2006 TexAQS/GoMACCS study. The results at the AQS surface sites show

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that both ARW-CMAQ and NMM-CMAQ reproduced day-to-day variations of observed $PM_{2.5}$ and captured the majority of observed $PM_{2.5}$ within a factor of 2 with the NMB value = −0.4 % for ARW-CMAQ and −18.4 % for NMM-CMAQ, especially for the concentration range of 10 to 35 μg m^{-3}. The domain daily mean $PM_{2.5}$ concentrations for the ARW-CMAQ are consistently about 17 % higher than those for the NNM-CMAQ during the 2006 TexAQS/GoMACCS period although both models performed much better at the urban sites than at the rural sites, with greater underpredictions at the rural sites. On the contrary, the ARW-CMAQ overestimated the observed $PM_{2.5}$ at the STN sites (most of them are located in urban areas) by 15 %, whereas the NMM-CMAQ underestimated by −16 %. The underestimation of $PM_{2.5}$ at the STN sites by the NMM-CMAQ mainly results from the underestimations of the SO_4^{2-}, NH_4^+ and TCM components, whereas the overestimation of $PM_{2.5}$ at the STN sites by the ARW-CMAQ results from the overestimations of SO_4^{2-}, NO_3^-, NH_4^+, and OTHER. Both models consistently underestimated the observed $PM_{2.5}$ at the IMPROVE sites (most of them are located in rural areas) by −1 % for the ARW-CMAQ and −19 % for the NMM-CMAQ. The greater underestimations of SO_4^{2-}, OC and EC by the NMM-CMAQ led to increased underestimation of $PM_{2.5}$ at the IMPROVE sites.

A comparison with the aircraft P-3 observations reveals that both models generally estimated SO_4^{2-} reasonably well on most days except on 9/16 and 9/21 but consistently overestimated NH_4^+ vertically except at layer 1, whereas both models systematically underestimated the NH_3 vertically for all observations. Both models performed reasonably well for observed SO_4^{2-} and NH_4^+ made on 9/13 and 9/25 over the Dallas-Fort Worth (DFW). Both models generally estimated HNO_3 reasonably well on most days except on 9/15, 9/29 and 10/6 in which both models had consistently high HNO_3 and the means of observed and modeled SO_2 concentrations are close with general overestimations near ground and general underestimations at high altitudes. Both models have reasonable performance for isoprene at the low altitudes (<2000 m) but completely missed the observed isoprene at the high altitudes (>2000 m). There is the consistent underestimations of terpenes by a factor of 2 to 4 by both models vertically

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from the low to high altitudes on most days especially at the high altitudes (>~1500 m). Both models captured the observed toluene well although both models had slight overestimation near the ground and underestimation at the high altitudes (>~2000 m). The systematical underestimation of terpene (by a factor of 2 to 4) suggests that the emission inventory may have been systematically low for terpene emissions. The time-series comparisons of the observations and models along the coast of southeastern Texas over the Gulf of Mexico show that both models captured the temporal variations and broad synoptic change seen in the observed HCHO and acetaldehyde with the means NMB <30 % along the ship track most of the time but underestimated terpenes, isoprene, toluene and SO_2 consistently. One of the reasons for these highly variable performances for each species is because of the complexity over the coastal region where there were land-sea contrast, the sea-breeze cycle, land-use differences and along-shore coastal irregularities.

In summary, ARW-CMAQ and NMM-CMAQ have similar model performances for $PM_{2.5}$, its chemical components and its related precursors as shown in this study. This is reasonable because both WRF-ARW and WRF-NMM are based on the same knowledge of state-of-science for meteorological processes although they use different dynamic cores in their implementations.

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Table 1. Comparison of ARW-CMAQ and NMM-CMAQ models for operational evaluation of daily $PM_{2.5}$ concentrations on the basis of the AQS data over the eastern United States.

		Domain Mean, $\mu g\,m^{-3}$			RMSE, $\mu g\,m^{-3}$		MB, $\mu g\,m^{-3}$		NMB (%)		NME (%)		*R*	
	Number	Obs	ARW	NMM	ARW	NMM	ARW	NMM	ARW	NMM	ARW	NMM	ARW	NMM
Rural	4103	12.8	10.0	8.1	6.9	7.9	−2.8	−4.7	−21.9	−36.9	38.8	45.5	0.63	0.60
Suburban	6554	13.6	13.6	11.2	7.7	7.7	0.0	−2.3	0.2	−17.2	39.4	40.9	0.56	0.52
Urban	5299	13.2	13.5	11.2	8.1	7.8	0.4	−2.0	2.8	−15.4	41.7	42.2	0.53	0.50
All data	19168	12.3	12.2	10.0	7.9	7.6	−0.1	−2.3	−0.4	−18.4	43.7	44.3	0.53	0.51

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Table 2. Comparison of ARW-CMAQ and NMM-CMAQ models for $PM_{2.5}$ and its components for each network over the eastern United States during the 2006 TexAQS/GoMACCS period.

	CASTNet					IMPROVE						STN				
	SO_4^{2-}	NH_4^+	NO_3^-	SO_2	TotS	$PM_{2.5}$	SO_4^{2-}	NO_3^-	OC	EC	TC	$PM_{2.5}$	SO_4^{2-}	NH_4^+	NO_3^-	TC
	ARW-CMAQ															
Mean (Obs)	4.16	1.26	0.32	0.72	2.42	7.19	2.48	0.22	1.24	0.31	1.55	13.49	3.86	1.32	0.56	4.32
Mean (Model)	3.74	1.23	0.47	1.45	3.31	7.14	2.88	0.38	1.11	0.28	1.38	15.53	4.90	1.91	1.12	3.23
Number	500	500	500	500	500	1648	1169	1169	1628	1628	1628	1816	1945	1945	1854	1971
correlation	0.88	0.82	0.30	0.73	0.81	0.52	0.64	0.35	0.30	0.48	0.37	0.30	0.57	0.45	0.36	0.29
MB	−0.41	−0.03	0.15	0.72	0.89	−0.05	0.40	0.16	−0.13	−0.04	−0.17	2.04	1.04	0.59	0.56	−1.09
RMSE	1.46	0.52	0.60	1.09	1.58	6.25	2.62	0.92	1.27	0.58	1.71	11.10	3.38	1.49	1.54	2.74
NMB (%)	−9.9	−2.5	46.7	99.4	36.8	−0.7	16.3	71.4	−10.7	−11.8	−10.9	15.1	27.0	100.6	44.8	−25.1
NME (%)	24.5	29.9	115.7	105.6	45.3	56.1	64.2	165.0	65.5	67.4	63.1	57.2	62.2	159.4	80.0	47.8
	NMM-CMAQ															
Mean (Obs)	4.16	1.26	0.32	0.72	2.42	7.19	2.48	0.22	1.24	0.31	1.55	13.49	3.86	1.32	0.56	4.32
Mean (Model)	2.94	0.99	0.43	1.36	2.93	5.85	2.04	0.37	1.00	0.22	1.22	11.32	3.33	1.33	0.74	2.52
Number	500	500	500	500	500	1648	1169	1169	1628	1628	1628	1816	1945	1945	1854	1971
correlation	0.89	0.83	0.23	0.77	0.83	0.61	0.77	0.39	0.42	0.53	0.46	0.35	0.66	0.54	0.36	0.37
MB	−1.22	−0.27	0.10	0.64	0.50	−1.34	−0.44	0.15	−0.24	−0.09	−0.33	−2.17	−0.53	0.01	0.19	−1.80
RMSE	1.98	0.60	0.52	0.93	1.20	5.02	1.93	0.77	1.06	0.44	1.38	9.53	2.50	1.03	1.00	2.75
NMB (%)	−29.3	−21.6	32.2	87.9	20.8	−18.6	−17.7	69.5	−19.7	−28.4	−21.5	−16.1	−13.7	0.4	33.3	−41.8
NME (%)	33.0	32.9	103.3	94.5	34.1	45.7	43.9	157.9	56.5	60.2	54.5	46.4	43.6	53.0	106.5	52.9

* The unit of Mean, MB, RMSE is $\mu g\,m^{-3}$, and TotS is total sulfur (SO_4^{2-} + SO_2) concentrations ($\mu g\ S\ m^{-3}$).

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Table 3. Flight Observation Summary for WP-3 aircraft for PM during the 2006 TexAQS/GoMACCS study.

Date	Observation summary for WP-3*
9/13	Dallas emission characterization and chemical processing, mean flow wind speed is 5 $m\,s^{-1}$ with northerly wind, takeoff at 10:45 and landing at 16:45 (LST)
9/15	Houston Urban, Parish power plant, Isolated refineries, light winds, Emission characterization, chemical processing, mean flow wind speed is 4.5 $m\,s^{-1}$ with southeasterly wind, takeoff at 09:50: and landing at 16:20 (LST)
9/16	Houston emission characterization and chemical processing, NE Texa power plants and aged Houston plume, takeoff at 9:55 and landing at 16:30 (LST)
9/19	Houston Urban, Parish power plant, Isolated refineries, flow from the NE, Emission characterization, chemical processing, mean flow wind speed is 7.5 $m\,s^{-1}$ with northeasterly wind, takeoff at 09:50 and landing at 16:20 (LST)
9/20	Beaumont Port Arthur, Houston Urban, Parish power plant, Isolated refineries, emission characterization, chemical processing, mean flow wind speed is 5.0 $m\,s^{-1}$ with easterly wind, takeoff at 09:55 and landing at 16:15 (LST)
9/21	Houston Urban and Industrial, Parish power plant, emission characterization, chemical processing, mean flow wind speed is 9.5 $m\,s^{-1}$ with southerly wind, takeoff at 09:50 and landing at 16:25 (LST)
9/25	Dallas, Parish power plant, Big Brown and Limestone power plants, GMD tower, emission characterization, chemical processing, mean flow wind speed is 3.5 $m\,s^{-1}$ with northerly wind, takeoff at 09:45 and landing at 16:25 (LST)
9/27	Houston Urban & Industrial, Parish power plant, Beaumont-Port Arthur, emission characterization, chemical processing, mean flow wind speed is 3.5 $m\,s^{-1}$ with southerly wind, takeoff at 12:45 and landing at 17:55 (LST)
9/29	Houston Urban & Industrial, Parish power plant, Emission characterization, chemical processing into the night, mean flow wind speed is 7.0 $m\,s^{-1}$ with southeasterly wind, takeoff at 13:45 and landing at 20:10 (LST)
10/5	Houston Urban & Industrial, Parish power plant, Chemical processing and transport, light winds from the northeasterly, takeoff at 9:50 and landing at 16:20 (LST)
10/6	Houston Urban & Industrial, Parish power plant, Victoria and Seadrift, chemical processing and transport, winds from the northeasterly, takeoff at 09:50 and landing at 16:00 (LST)

* Based on flight information presented at http://esrl.noaa.gov/csd/tropchem/2006TexAQS/P3/index.html and McKeen et al. (2009).

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Table 4. Comparison of layer means of $PM_{2.5}$ (SO_4^{2-} and NH_4^+) and its related precursors from observations and model (ARW-CMAQ, NMM-CMAQ) on the basis of all P3 aircraft measurements during the 2006 TexAQS/GoMACCS.

		SO_4^{2-}		NH_4^+		HNO_3		NH_3		SO_2		isoprene		toluene		terpenes	
Layer	Height	obs	Mod	obs	Mod	obs	Mod	obs	Mod	obs	Mod	obs	Mod	obs	Mod	obs	Mod
ARW-CMAQ																	
1	38	2.80	1.69	0.82	0.72	1.75	2.20	2.37	1.12	2.74	3.63	475.0	304.4	355.5	518.8	87.3	41.2
2	79	0.95	0.65	1.40	1.68	1.74	2.30	2.04	0.97	2.62	3.84	315.4	272.1	260.1	462.7	48.0	40.5
3	118	1.03	2.13			1.92	2.31	2.07	0.76	2.52	3.40	185.3	161.2	358.8	251.9	49.4	18.5
4	158					2.02	2.33	2.39	0.71	2.68	2.84	270.3	173.6	408.9	322.2	36.4	16.8
5	239	2.93	3.25	1.15	1.42	1.84	2.22	2.06	0.55	2.15	2.12	237.2	163.9	247.5	174.9	33.0	12.9
6	319	3.22	3.07	1.22	1.57	1.79	2.60	1.91	0.42	2.05	1.46	209.5	149.4	143.5	129.1	33.3	9.5
7	401	3.31	3.33	0.85	1.10	2.12	2.49	1.43	0.71	1.68	1.36	298.7	300.4	173.6	137.3	41.6	26.4
8	482	2.91	2.81	0.76	0.97	2.02	2.49	1.48	0.58	1.97	1.65	188.8	154.2	169.5	140.9	35.2	11.8
9	565	3.19	2.85	0.80	1.02	1.80	2.44	1.25	0.41	1.73	1.36	157.5	142.3	126.5	100.2	31.1	9.0
10	648	2.83	2.89	0.54	0.89	1.69	2.33	1.15	0.48	1.52	1.02	172.3	139.9	127.4	95.3	32.4	10.0
11	731	2.63	3.03	0.62	0.86	1.61	1.99	1.13	0.54	1.48	0.96	158.9	156.8	120.5	84.5	34.3	11.5
12	815	2.68	2.76	0.60	0.93	1.64	2.04	1.09	0.49	1.45	1.01	127.7	128.1	121.9	76.5	31.0	9.6
13	985	2.45	3.20	0.47	0.80	1.56	1.99	1.00	0.50	1.34	1.11	126.7	109.2	95.5	89.5	33.4	7.7
14	1158	2.99	2.90	0.54	0.96	1.59	2.48	0.80	0.49	1.54	1.19	138.9	165.7	92.7	103.1	27.7	11.5
15	1333	2.84	2.49	0.57	0.96	1.25	2.08	0.64	0.42	0.81	0.90	104.2	133.8	77.2	87.8	26.1	9.6
16	1511	2.13	2.18	0.71	0.92	1.01	1.65	0.53	0.32	0.71	0.67	62.5	58.5	46.4	54.5	24.8	3.8
17	1692	1.51	1.78	0.39	1.13	0.83	1.51	0.46	0.21	0.48	0.55	48.7	33.3	45.8	41.3	27.5	3.3
18	1968	1.85	2.52	0.50	0.68	0.70	1.32	0.39	0.20	0.41	0.51	35.9	25.6	39.7	32.4	19.5	1.7
19	2252	1.51	1.73	0.40	0.65	0.52	0.96	0.30	0.12	0.28	0.35	35.1	3.6	31.2	13.5	21.5	0.2
20	2643	2.31	2.53	0.39	0.47	0.39	0.77	0.24	0.05	0.25	0.23	29.8	0.6	22.4	10.4	17.4	0.0
21	3155	0.58	0.77	0.28	0.39	0.35	0.65	0.21	0.08	0.24	0.15	30.7	0.9	23.8	7.4	20.6	0.0
22	3695	1.57	0.81	0.41	0.47	0.26	0.46	0.18	0.01	0.25	0.07	35.2	0.1	25.0	5.5	21.8	0.0
23	4265			0.10	0.10	0.17	0.34	0.16	0.00	0.24	0.02	43.6	0.5	23.9	4.9	25.2	0.0
24	4872			1.00	0.16	0.13	0.28	0.06	0.00	0.27	0.02	42.6	1.4	22.2	2.4	21.9	0.1
25	5523					0.08	0.22	0.15	0.00	0.30	0.01	45.4	1.4	21.5	2.1	23.3	0.2
mean		2.30	2.35	0.66	0.86	1.23	1.70	1.02	0.41	1.27	1.22	143.0	111.2	127.2	118.0	32.1	10.2
NMM-CMAQ																	
1	38	2.61	1.10	0.82	0.63	1.74	2.22	2.37	1.06	2.72	4.11	471.0	302.0	354.0	547.0	83.7	45.9
2	116	1.10	1.56	1.40	1.64	1.88	2.36	2.04	0.76	2.54	3.69	225.0	161.0	386.0	308.0	48.3	18.4
3	197	2.58	2.13			1.88	2.46	2.29	0.63	2.27	2.73	259.0	139.0	266.0	203.0	34.5	12.5
4	282	3.07	3.09	0.94	1.25	1.88	2.48	1.93	0.46	1.91	1.63	204.0	118.0	146.0	112.0	32.7	7.5
5	372	2.31	2.50	0.73	1.12	2.01	2.72	1.46	0.49	1.73	1.22	276.0	221.0	176.0	118.0	38.5	21.7
6	470	2.68	2.67	0.79	1.00	2.05	2.59	1.46	0.51	1.97	1.36	189.0	132.0	165.0	122.0	34.8	11.1
7	578	2.78	2.69	0.80	1.10	1.64	2.55	1.19	0.43	1.65	1.19	188.0	152.0	129.0	96.7	32.5	11.9
8	699	2.03	2.79	0.54	0.91	1.74	2.44	1.16	0.44	1.60	1.11	149.0	113.0	138.0	102.0	31.7	9.2
9	847	2.55	2.56	0.59	0.97	1.57	2.02	1.06	0.40	1.33	0.91	128.0	104.0	108.0	80.6	39.0	8.5
10	1049	2.49	2.65	0.45	0.85	1.65	2.73	0.91	0.41	1.48	1.15	138.0	106.0	103.0	116.0	26.7	8.1
11	1301	3.55	2.79	0.60	1.09	1.22	2.26	0.64	0.32	0.92	0.78	104.0	85.7	71.9	71.6	28.0	6.4
12	1753	1.32	2.00	0.46	0.99	0.84	1.42	0.46	0.21	0.52	0.43	47.7	37.5	44.8	34.2	25.3	3.3
13	2283	1.70	1.77	0.42	0.69	0.53	0.89	0.29	0.09	0.31	0.22	32.8	9.3	31.7	14.3	19.1	0.8
14	2898	1.72	1.04	0.39	0.57	0.36	0.61	0.22	0.06	0.25	0.16	31.0	2.0	24.0	6.8	19.7	0.1
15	3619			0.37	0.46	0.25	0.35	0.16	0.01	0.26	0.10	34.9	0.1	25.3	2.1	21.9	0.0
16	4460			0.55	0.11	0.16	0.23	0.06	0.00	0.25	0.03	46.6	0.0	23.0	1.3	24.1	0.0
17	5413					0.11	0.15	0.12	0.00	0.29	0.01	39.6	0.0	23.4	0.6	22.9	0.0
mean		2.32	2.24	0.66	0.89	1.26	1.79	1.05	0.37	1.29	1.22	150.8	99.0	130.3	113.9	33.1	9.73

* $\mu g\,m^{-3}$: SO_4^{2-} and NH_4^+; ppbv: HNO_3, NH_3, SO_2; pptv: isoprene, toluene, terpenes; m: height.

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Table 5. Comparison of observations and models (NMM-CMAQ and ARW-CMAQ) for different gaseous species (SO_2, NH_3, acetaldehyde, formaldehyde, isoprene, toluene and terpenes) on the basis of all ship measurements over the Gulf of Mexico during the 2006 TexAQS (all units are ppbv).

	Mean ± standard deviation			NMB (%)	
	Obs	NMM-CMAQ	ARW-CMAQ	NMM-CMAQ	ARW-CMAQ
SO_2	3.77±9.83	2.66±3.94	2.12±3.37	−29.5	−43.7
NH_3	0.41±1.73	0.53±1.08	0.50±1.14	29.0	22.2
Acetaldehyde	1.00±1.06	1.35±1.37	1.29±1.31	34.6	29.0
Formaldehyde	2.01±2.03	2.45±1.88	2.28±1.69	21.6	13.0
Isoprene	0.35±0.57	0.19±0.34	0.23±0.50	−45.6	−34.0
Toluene	0.61±1.40	0.41±0.53	0.37±0.60	−32.8	−38.8
Terpenes	0.25±0.23	0.06±0.11	0.05±0.10	−74.2	−80.9

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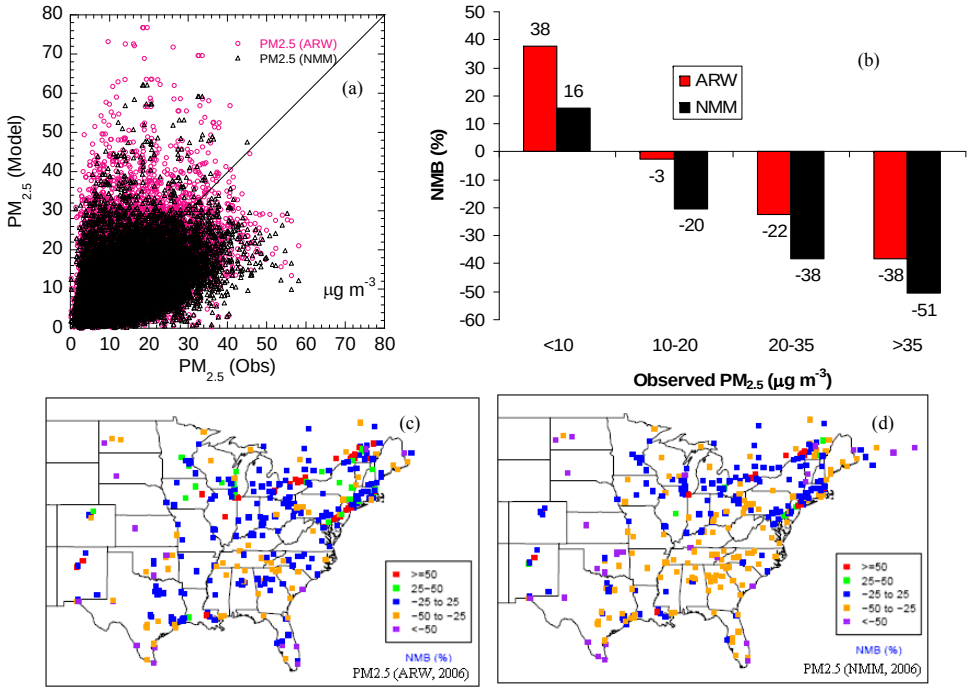

Fig. 1. Comparison of the modeled (ARW-CMAQ, NMM-CMAQ) and observed daily $PM_{2.5}$ concentrations at the AIRNow monitoring sites **(a)** scatterplot (ppbv); **(b)** the NMB values of each model as a function of the observed daily $PM_{2.5}$ concentration ranges; spatial distributions of NMB for **(c)** ARW-CMAQ and **(d)** NMM-CMAQ during the period 5 August and 7 October 2006.

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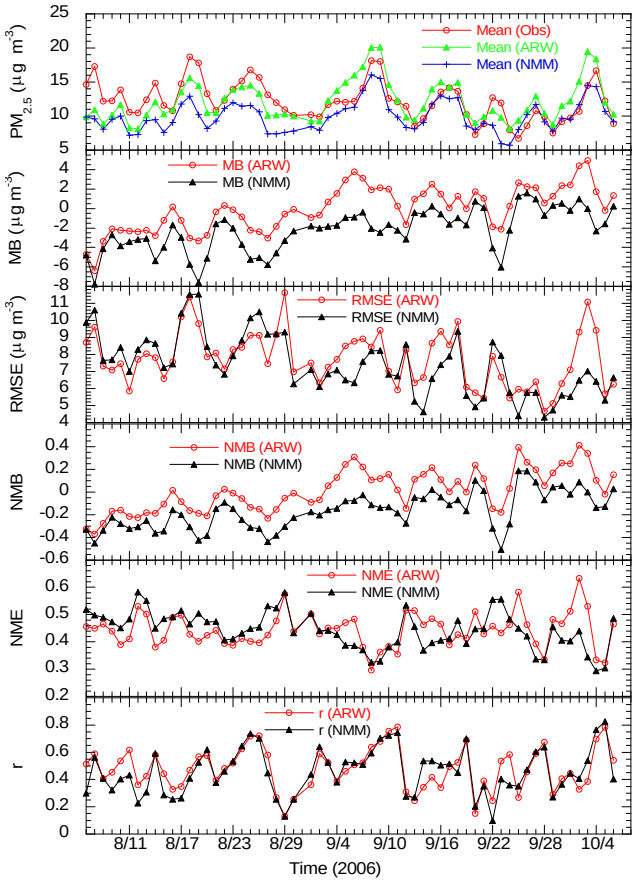

Fig. 2. Comparison of daily variations of the values of domain-wide mean, MB, RMSE, NMB, NME and correlation coefficient (r) for the daily $PM_{2.5}$ mass concentrations at the AIRNow monitoring sites for ARW-CMAQ and NMM-CMAQ simulations.

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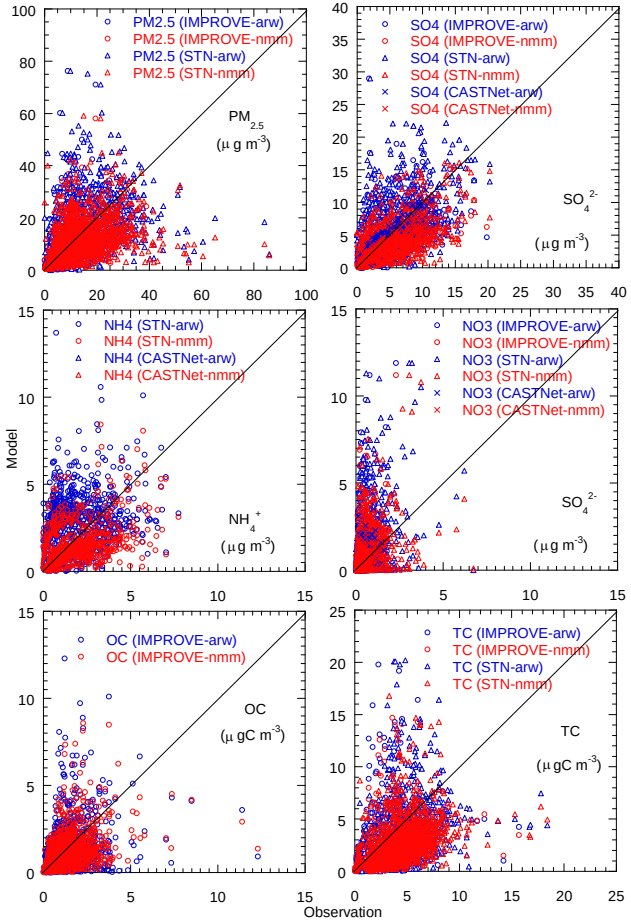

Fig. 3a. Comparison of observed and modeled (ARW-CMAQ and NMM-CMAQ) $PM_{2.5}$ and its chemical composition at the IMPROVE, STN and CASTNet sites during the 2006 Tex-AQS/GoMACCS period.

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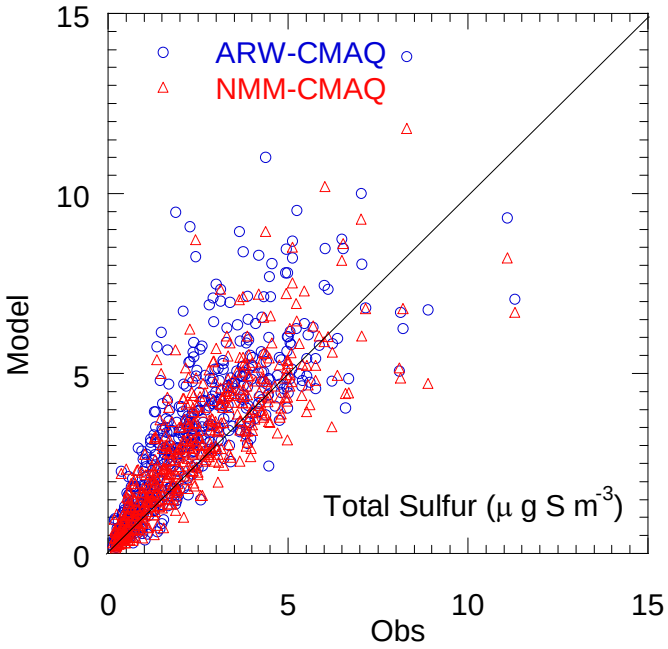

Fig. 3b. Comparison of observed and modeled (ARW-CMAQ and NMM-CMAQ) total sulfur ($SO_4^{2-} + SO_2$) concentrations at the CASTNet sites during the 2006 TexAQS/GoMACCS period.

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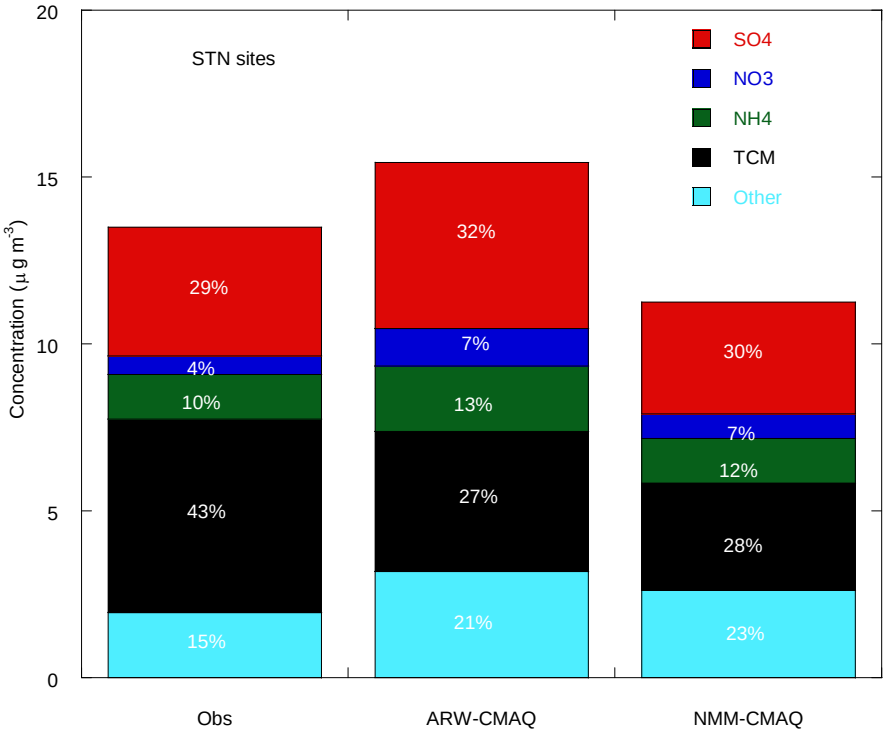

Fig. 4. Comparison of stacked bar-plots for observed and modeled (ARW-CMAQ, NMM-CMAQ) $PM_{2.5}$ chemical composition at the STN sites during the 2006 TexAQS/GoMACCS period. The percentages represent the fractions of each composition for $PM_{2.5}$.

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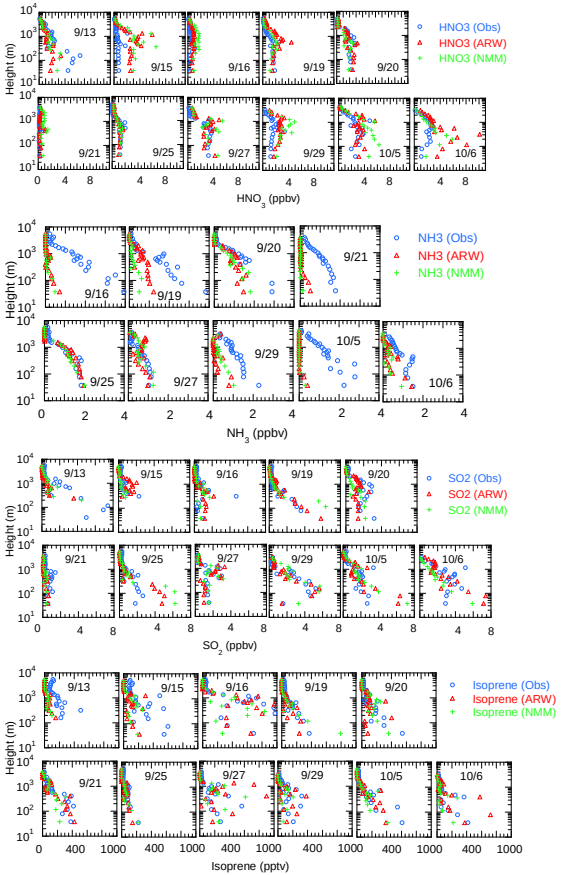

Fig. 5. Comparison of composite vertical distributions of observed and modeled (ARW-CMAQ and NMM-CMAQ) HNO_3, NH_3, SO_2, Isoprene, toluene, terpenes, $PM_{2.5}$ SO_4^{2-} and NH_4^+ along the aircraft transects of P-3 during the 2006 TexAQS/GoMACCS.

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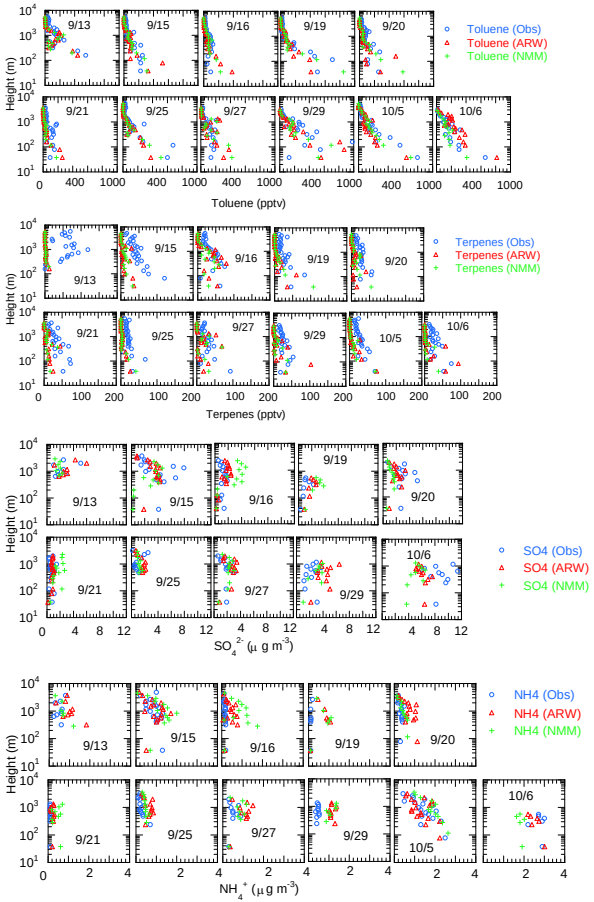

Fig. 5. Continued.

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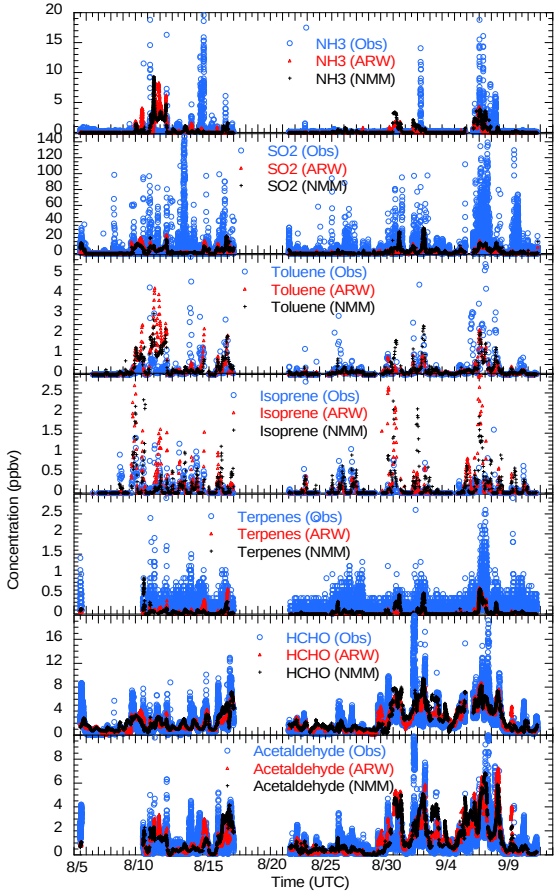

Fig. 6. Time series of observations and model predictions (NMM-CMAQ and ARW-CMAQ) for difference species on the basis of ship measurements over the Gulf of Mexico during the 2006 TexAQS/GoMACCS period.

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