

Modeling urban and regional aerosols—Application of the CMAQ-UCD Aerosol Model to Tampa, a coastal urban site

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Abstract

The University of California at Davis (UCD) aerosol module, an internally mixed, sectional aerosol model with dynamic mass transfer between the gas and particle phases, has been coupled to the Community Multiscale Air Quality (CMAQ) model. This paper describes the application of the CMAQ-UCD model to simulate air quality in Tampa, a large city with a population of 2M on the west coast of Florida, USA. Modeled aerosol size and composition distributions are evaluated against size-segregated ambient measurements of SO_4^{2-} , NH_4^+ , NO_3^- , Na^+ , and Cl^- collected at three Tampa-area sites during May 2002, and against semi-continuous HNO_3 and total aerosol SO_4^{2-} , NH_4^+ , NO_3^- , and Cl^- measurements collected at a single site. Sea-salt emissions over the open ocean and the surf zone are parameterized as a function of modeled wind speed and relative humidity. Modeled total aerosol sulfate and ammonium concentrations and size distributions agree with measurements, with an overall normalized mean bias (NMB) of 2% and -23% and normalized mean error (NME) of 46% and 38%, respectively, and correctly identifying the size bin in which the peak concentration is observed. Sea-salt size distributions are also simulated well, with the distribution dominated by the coarse mode and total aerosol sodium and chloride NMB of -2% and 17% and NME of 32% and 38%. Though the model correctly identifies that nitrate is predominantly in the coarse ($D_p > 2.5 \mu\text{m}$) size sections, aerosol nitrate concentrations are underpredicted by a factor of two. The availability of highly time-resolved measurements provides a unique opportunity to evaluate the model's partitioning of total nitrate and the simulation of chloride depletion as a function of particle size.

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1. Introduction

Atmospheric particulate matter (PM) is of interest primarily because of the well-documented association of high ambient concentrations with increases in human mortality (e.g., Dockery et al.,

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1993; Samet et al., 2000). PM also has the potential for enhancing or mitigating global climate change via radiative forcing (IPCC, 2001) as well as impairing visibility in both polluted urban environments (Kleeman et al., 2001) and in scenic locations such as national parks (NRC, 1993).

Certain ecosystems are particularly sensitive to nitrate deposition, due to the effects of acidification or eutrophication (Paerl, 1995). In coastal environments, coarse sea-salt particles may act as reactive sinks for nitric acid (HNO_3) via the reaction $\text{NaCl} + \text{HNO}_3 \rightarrow \text{NaNO}_3 + \text{HCl}$, providing the principal source of gas-phase HCl (Elderling et al., 1991; Pakkanen, 1996; Gard et al., 1998; Knipping and Dabdub, 2003). However, in many regional air quality models developed to date, sea salt has been treated as chemically inert, having no interaction with gas-phase HNO_3 (Eder and Yu, 2006; Foltescu et al., 2005; Smyth et al., 2006; Gaydos et al., 2007). In some other studies in which the models did simulate sea-salt aerosol dynamics, results suffered from having relatively crude estimates of sea-salt emissions or boundary conditions (Lurmann et al., 1997; Meng et al., 1998; Sun and Wexler, 1998b; Zhang et al., 2004).

Recently, a new aerosol module, the UCD aerosol module, has been developed and coupled to CMAQ (Zhang and Wexler, 2008). The UCD aerosol module is a fully dynamic, internally mixed, sectional model with simplified thermodynamics based on the Aerosol Inorganic Model (AIM) (Sun and Wexler, 1998a; Wexler and Clegg, 2002). This paper describes the application of CMAQ-UCD to simulate air quality in the coastal urban location of Tampa, Florida. Rather than assuming a constant sea-salt emission flux or boundary condition, we employ a parameterization of size-segregated sea-salt emissions based on modeled wind speed and relative humidity. Model predictions of aerosol sulfate (SO_4^{2-}), nitrate (NO_3^-), ammonium (NH_4^+), sodium (Na^+), and chloride (Cl^-) are compared against size-segregated measurements of atmospheric concentrations in this first evaluation of the CMAQ-UCD model. We note that the purpose of this study is not to evaluate model performance broadly against a network of air monitoring locations, as done recently for CMAQ (Eder and Yu, 2006) and PMCAMx (Gaydos et al., 2007). It has been observed that CMAQ performs relatively poorly at coastal locations (Eder and Yu, 2006), particularly for aerosol nitrate (Smyth et al., 2006). Here we focus on a coastal location with

available observations to examine CMAQ-UCD's ability to simulate the interaction between marine aerosol and urban pollution.

2. Model configuration

For a complete description of the Community Multiscale Air Quality-University of California, Davis (CMAQ-UCD) model, see Zhang and Wexler (2008); only a brief summary of key model features is presented here. CMAQ-UCD is built onto the framework of CMAQ version 4.4 (Byun and Ching, 1999; Byun and Schere, 2006). However, in place of the CMAQ modal aerosol module (Binkowski and Roselle, 2003), CMAQ-UCD uses a sectional aerosol module with 12 species in each size bin, including SO_4^{2-} , NH_4^+ , NO_3^- , Na^+ , Cl^- , elemental carbon, primary organic aerosol, biogenic secondary organic aerosol (SOA), anthropogenic SOA, mineral dust, water, and hydrogen ion. In the CMAQ aerosol model of Binkowski and Roselle (2003), the gas phase and fine PM are assumed to be in thermodynamic equilibrium, while coarse particles, including sea salt, are assumed to be inert. By contrast, CMAQ-UCD is fully dynamic, explicitly computing sea-salt thermodynamics and mass transport between the gas phase and each size section. Three gas-to-particle conversion schemes, termed replacement transport, coupled transport, and uncoupled transport, are utilized depending on the relative amounts of NH_4^+ , NO_3^- , and Cl^- present and whether the system is near acid neutrality. The equations governing aerosol dynamics are solved using an asynchronous time-stepping (ATS) technique (Zhang and Wexler, 2006), in which concentrations of slowly varying species are integrated using a larger timestep than species whose concentrations vary on a shorter timescale. Zhang and Wexler (2006) reported that the ATS method attains a solution 10–100 times faster than the Livermore solver for ordinary differential equations (LSODE) implementation of the Gear method while maintaining overall solution accuracy.

For this application, nine aerosol size sections were used, each spanning a factor of two in Stokes diameter, with the smallest ranging from 0.039 to 0.078 μm and the largest from 10 to 20 μm . CMAQ was configured to use the SAPRC99 gas-phase chemical mechanism (Carter, 2000) and the Euler backward iterative solver. The modeling period was 21 April–3 June 2002. The outer modeling domain consisted of a 32 km \times 32 km horizontal grid over

the continental US with 21 vertical layers in a sigma coordinate system extending from the surface to 100 hPa. Boundary conditions for the 32 km simulation were computed from temporally invariant vertical concentration profiles as described by [Byun and Ching \(1999\)](#). A nested simulation was performed on an 8 km \times 8 km grid covering the Southeast US (see [Fig. 1a](#)), including the entire Tampa airshed and portions of nine surrounding states to track regional emissions. Initial and

boundary conditions for the 8 km simulation were taken from the 32 km simulation. Results are presented from the 8 km simulation only.

Tampa is a city of 2M people located on the west coast of Florida. The Bay Region Atmospheric Chemistry Experiment (BRACE) ([Atkeson et al., 2007](#)) was specifically designed to answer questions related to Tampa-area nitrogen emissions, transformation, and deposition to Tampa Bay. As part of BRACE, a large field measurement campaign involving more than a dozen research groups was conducted in May 2002, in which the concentrations of more than 100 gas- and aerosol-phase compounds were measured at four sites, while instruments aboard aircraft were used to characterize urban and power plant plumes aloft. Extensive meteorological observations, including three wind profilers and radio acoustic sounding systems (RASS) and an instrumented overwater tower in the Bay, were made in support of BRACE modeling objectives. Since accurate emissions and meteorological input data are critical to air quality model performance, the existence of this rich data set makes BRACE a good candidate for modeling the complex interaction between marine aerosol and pollutants in the urban atmosphere.

The 5th generation Penn State/NCAR Mesoscale Model (MM5) v3.6 ([Grell et al., 1994](#)) was used to simulate the meteorology that drove the air quality model. The meteorological model was configured with 30 vertical layers, with 11 layers being in the lowest 1000 m and a surface layer nominally 38 m deep, the Pleim-Xiu planetary boundary layer (PBL) and land-surface schemes, the Grell cloud parameterization schemes, the rapid radiative transfer model (RRTM), and the Reisner II microphysics scheme. The model employed analysis and observation nudging of temperature and moisture at the surface and aloft, and of winds aloft, as well as utilizing sea surface temperature data processed from the NOAA GOES satellite.

Area source emissions are based on the U.S. Environmental Protection Agency (USEPA) 1999 National Emissions Inventory (NEI) v3, which were projected to 2002. Ammonia emissions were corrected with results from inverse modeling as described by [Gilliland et al. \(2006\)](#). Biogenic sources are computed with the Biogenic Emissions Inventory System (BEIS) v3.10. Mobile source emissions are processed using the USEPA mobile source emissions model, v5B (MOBILE5B). Point sources are calculated from the 2001 USEPA Clean Air

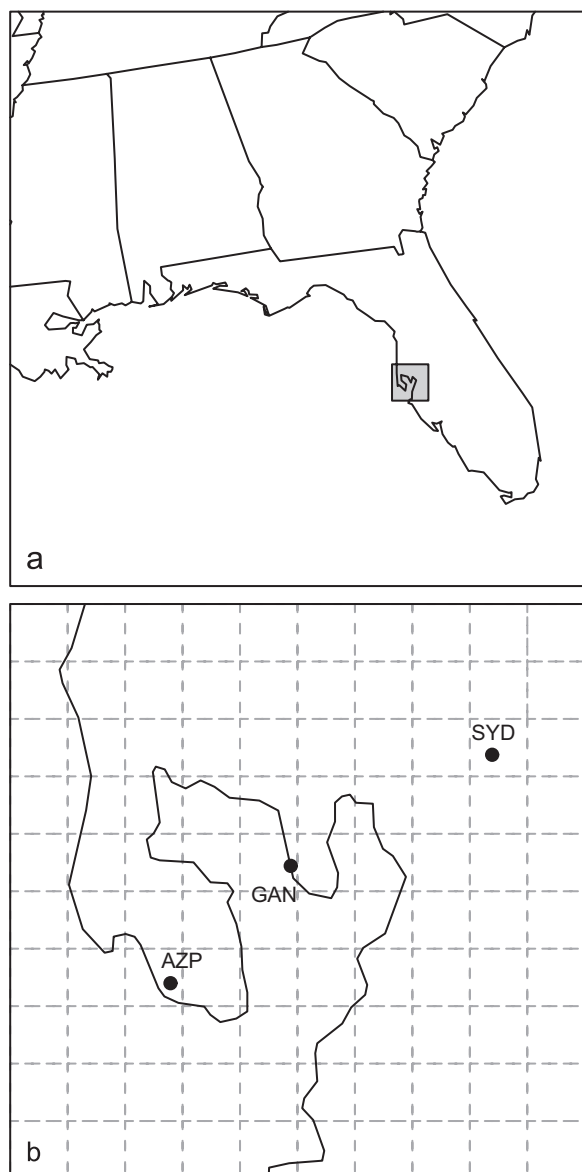


Fig. 1. (a) Entire BRACE 8 km modeling domain. Shaded portion represents 80 km \times 80 km region surrounding Tampa. (b) Zoom of shaded region in (a), showing observational sites at Azalea Park (AZP), Gandy Bridge (GAN), and Sydney (SYD).

Interstate Rule emissions inventory, adjusted by 2002 continuous emission monitoring (CEM) data where available. Dennis et al. (2007) assigned uncertainty values for each major NO_x emissions source sector in deriving an overall NO_x emissions uncertainty of ±35–57% for the eastern US. Since Tampa-area NO_x emissions have a disproportionately large contribution from the utilities sector, whose emissions are more certain than the other sectors, the overall NO_x emissions uncertainty for this application is probably closer to ±35%. Combining the agreement obtained by Gilliland et al. (2003), between NH_x (NH₃ + NH₄⁺) observations in the eastern US and CMAQ-modeled NH_x when using inverse modeling-adjusted NH₃ emissions, with their own modeling results showing the damped response of NH_x to changed NH₃ emissions, Dennis et al. (2007) report that NH₃ emissions are uncertain to a factor of 0.64–1.56.

Size-dependent emission fluxes of sea-salt cations, chloride, and sulfate from the open ocean and surf zone are calculated using the parameterizations of Gong (2003) and de Leeuw et al. (2000), respectively, with relative humidity-dependent size adjustments based on the polynomial expansions of Zhang et al. (2005). To facilitate acidity and charge balance calculations, all cations in sea salt are treated as sodium in the emission input, and then rescaled during postprocessing. The width of the surf zone is assumed to be 50 m (Petelski and Chomka, 1996). We note that this is not the first time such a parameterization has been employed in a chemical transport model. Jacobson (1997) used an earlier parameterization from Monahan et al. (1983) for particles between 0.6 and 34 μm diameter, and a further parameterization for ocean spume drops. Kleeman et al. (2001) used the same surf zone parameterization of de Leeuw et al. (2000) used here, along with fixed boundary conditions from measurements at an upwind island site to represent sea-salt particles produced over the open ocean. However, neither Jacobson (1997) nor Kleeman et al. (2001) evaluated the modeled size distributions of supermicron Na⁺ and Cl⁻, as will be presented in this work. Knipping and Dabdub (2003) used a similar sea-salt generating function to that employed here, as well as a comprehensive chlorine chemical reaction mechanism, but their focus was the effect of sea-salt-derived chlorine on ozone rather than on the aerosol size distribution. Finally, Spyridaki et al. (2006) simulated aerosol dynamics in the eastern Mediterranean using a similar hourly

sea-salt emission parameterization with the UAM-AERO modeling system.

3. Observations

Observations used here for model evaluation include airborne PM that was size-segregated by micro-orifice uniform deposit impactors (MOUDIs) at three Tampa-area sites as shown in Fig. 1b. Samples were collected for 23 h (0700–0600 LST) at 30 L min⁻¹ on 47-mm PTFE filters and analyzed by ion chromatography for sulfate, ammonium, nitrate, sodium, and chloride (Evans et al., 2004). Other analytes that were measured by Evans et al. (2004) (e.g., K⁺, Mg²⁺, and Ca²⁺) are not tracked explicitly in the CMAQ-UCD model, so they are not discussed further here. There were two co-located MOUDI instruments at the Sydney site. Two of the four MOUDIs had 10 fractionated stages, while the other two had eight stages. In all cases, the stages ranged from 0.056 to 18 μm aerodynamic diameter. Samples were collected on 15 days (14 at Sydney) between 4 May and 2 June 2002, resulting in a total of 58 MOUDI samples.

In addition, total (aerodynamic diameter 50% cut point ~12.5 μm) aerosol sulfate, ammonium, nitrate, and chloride were analyzed semi-continuously (15-min resolution) at a single site in Sydney, Florida, using a parallel plate wetted denuder followed by a soluble particle collector (Dasgupta et al., 2007). Finally, gas-phase HNO₃ was measured continuously by a denuder difference technique (Arnold et al., 2007).

4. Results

4.1. Predicted and measured total PM concentrations

Predicted average total concentrations (summed over all size bins) of aerosol sulfate, ammonium, nitrate, sodium, and chloride are compared to average MOUDI totals in Table 1. Statistics given are for correlation coefficient R , normalized mean bias, $\text{NMB} = \sum(C_{\text{mod}} - C_{\text{obs}}) / \sum C_{\text{obs}} \times 100\%$, normalized mean error, $\text{NME} = \sum |C_{\text{mod}} - C_{\text{obs}}| / \sum C_{\text{obs}} \times 100\%$, and root mean squared error, $\text{RMSE} = \sqrt{(1/n) \sum (C_{\text{mod}} - C_{\text{obs}})^2}$. Scatterplots of predicted and observed total inorganic aerosol concentrations are shown in Fig. 2. The daily totals of the two co-located MOUDIs at the Sydney site

Table 1
Mean observed (summed over all MOUDI stages) and model-predicted inorganic aerosol concentrations ($\mu\text{g m}^{-3}$) at three sites near Tampa, Florida

Species	Observed	Predicted	R^a	NMB ^b	NME ^c	RMSE ^d
<i>Azalea Park</i>						
Sulfate	4.03	3.91	0.41	−3	47	2.6
Ammonium	1.23	0.86	0.45	−30	39	0.6
Nitrate	1.96	0.89	0.33	−54	54	1.3
Sodium	1.62	1.37	0.58	−16	33	0.6
Chloride	1.93	1.90	0.60	−1	31	0.9
<i>Gandy Bridge</i>						
Sulfate	4.08	4.69	0.40	15	52	3.2
Ammonium	1.30	1.02	0.47	−21	31	0.6
Nitrate	1.74	1.04	0.20	−40	51	1.0
Sodium	1.46	1.61	0.55	10	36	0.6
Chloride	1.72	2.22	0.64	29	45	1.0
<i>Sydney</i>						
Sulfate	3.13	2.84	0.26	−9	36	1.4
Ammonium	1.04	0.85	0.15	−18	44	0.6
Nitrate	1.51	0.71	0.70	−53	53	0.9
Sodium	1.14	1.17	0.76	2	26	0.4
Chloride	1.31	1.69	0.75	29	40	0.7
<i>All sites</i>						
Sulfate	3.76	3.83	0.42	2	46	2.5
Ammonium	1.19	0.91	0.39	−23	38	0.6
Nitrate	1.74	0.88	0.35	−49	53	1.1
Sodium	1.41	1.38	0.61	−2	32	0.6
Chloride	1.66	1.94	0.64	17	38	0.8

^aPearson correlation coefficient.

^bNormalized mean bias, percent.

^cNormalized mean error, percent.

^dRoot mean squared error, $\mu\text{g m}^{-3}$.

are highly correlated (R from 0.91 to 0.98), which gives confidence to the observations; we have averaged the measurements from the two instruments at Sydney in Fig. 2. With respect to the observations, sulfate concentration predictions are essentially unbiased (NMB = 2%), with an overall correlation $R = 0.42$ and with 77% of predicted concentrations within a factor of two of the observations. Ammonium concentrations are somewhat underpredicted, with NMB ranging from −18% at Sydney to −30% at Azalea Park. The overall correlation R is 0.39, and 77% of predicted concentrations are within a factor of two of the observations. These results are reasonably good, considering the significant uncertainty in ammonia emissions, and are in line with previous model evaluations of CMAQ (Eder and Yu, 2006).

Predicted sodium concentrations agree very well with the MOUDI measurements, with little bias

(overall NMB −2%) and 93% of predictions accurate within a factor of two. With correlation coefficients ranging from 0.55 to 0.76, there is actually less scatter in the Na^+ predictions than for SO_4^{2-} , which is typically the aerosol species that is easiest to model correctly. The normalized mean error (NME) of the sulfate predictions is from 36% to 52%, while for sodium it is 25–35%. The only source of sodium in the model is sea-salt emissions, which are a function of wind speed and relative humidity. After being emitted, the only processes affecting sodium are advection and removal by dry and wet deposition. In addition to these processes, modeling sulfate requires accurate simulation of in-cloud oxidation of SO_2 , and meteorological models have difficulty in accurately simulating clouds. The excellent agreement between predicted and measured sodium concentrations indicates that, on average, the model is correctly simulating sea-salt emissions, advective transport, and removal.

Modeled chloride concentrations are in fairly good agreement with observations, essentially unbiased at Azalea Park and with a NMB of 29% at the other two sites. Predictions are within a factor of two for 86% of the observations, and the overall correlation coefficient between measured and modeled chloride is 0.64. Like Na^+ , sea-salt emissions are the only source of Cl^- in the model. However, in addition to being affected by advection and wet and dry deposition, Cl^- can be removed via heterogeneous reaction with HNO_3 . The depletion of Cl^- due to displacement by NO_3^- will be investigated below.

Aerosol nitrate concentrations are consistently underpredicted at all sites. Normalized mean biases (NMBs) range from −40% at Gandy Bridge to −54% at Azalea Park, with an overall correlation coefficient of 0.35, and with only 39% of predictions within a factor of two of the observations. Particulate nitrate is one of the most difficult constituents to predict because it is sensitive to almost every physical and chemical process in the model including NO_x and VOC emissions, atmospheric transport, gas-phase chemistry, gas and particle deposition, and gas-particle phase partitioning. Possible causes of the underprediction of aerosol nitrate are discussed further below.

4.2. Predicted and measured size distributions

Modeled aerosol size distributions and speciated MOUDI measurements at the three sites are

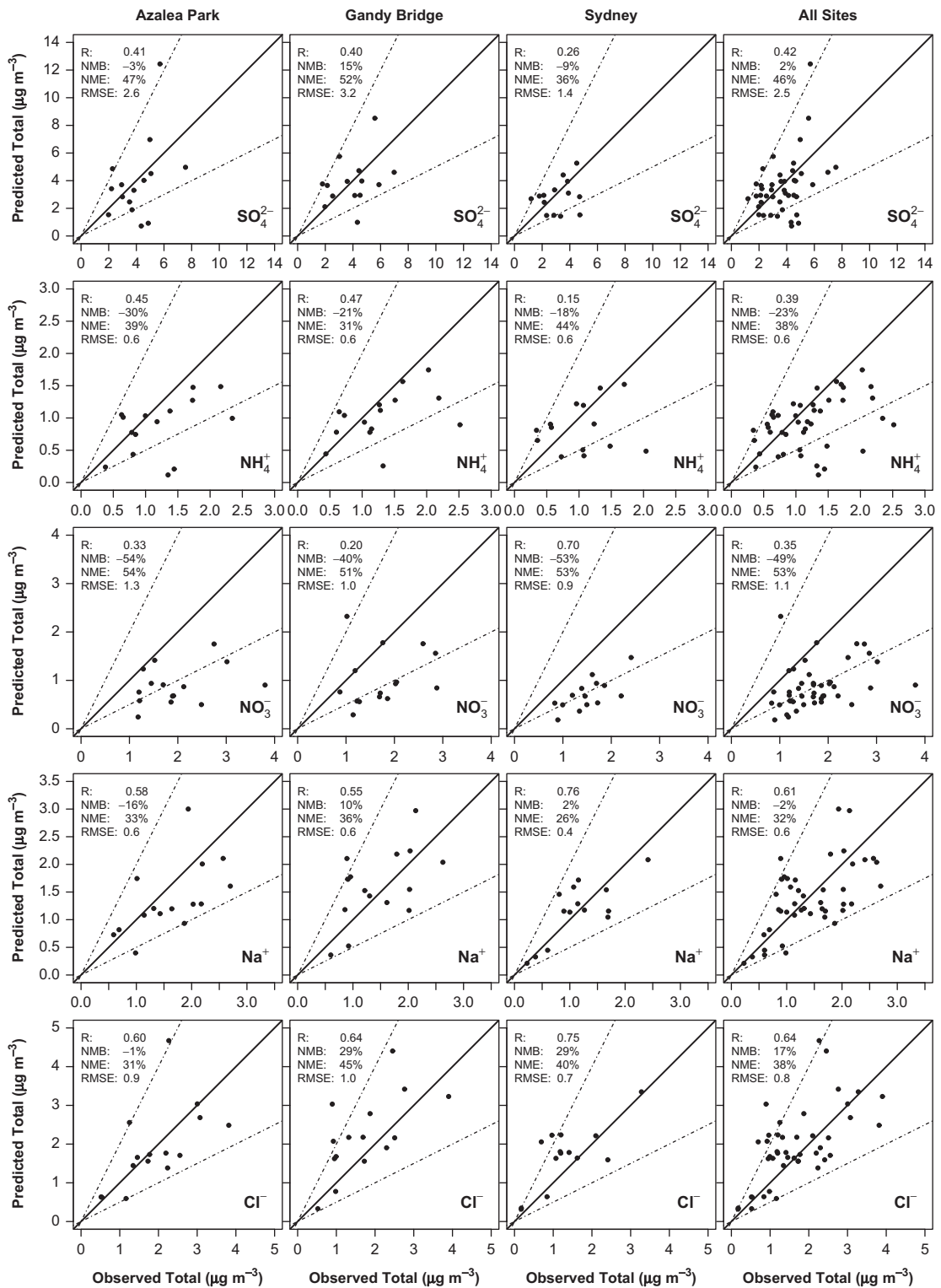


Fig. 2. Modeled total inorganic aerosol concentrations vs. 23-h MOUDI observations at three sites near Tampa during May 2002. For reference, solid line represents 1:1 ratio; dashed lines represent 1:2 and 2:1 ratios. Statistics given are for Pearson correlation coefficient (R), normalized mean bias (NMB), normalized mean error (NME), and root mean squared error (RMSE).

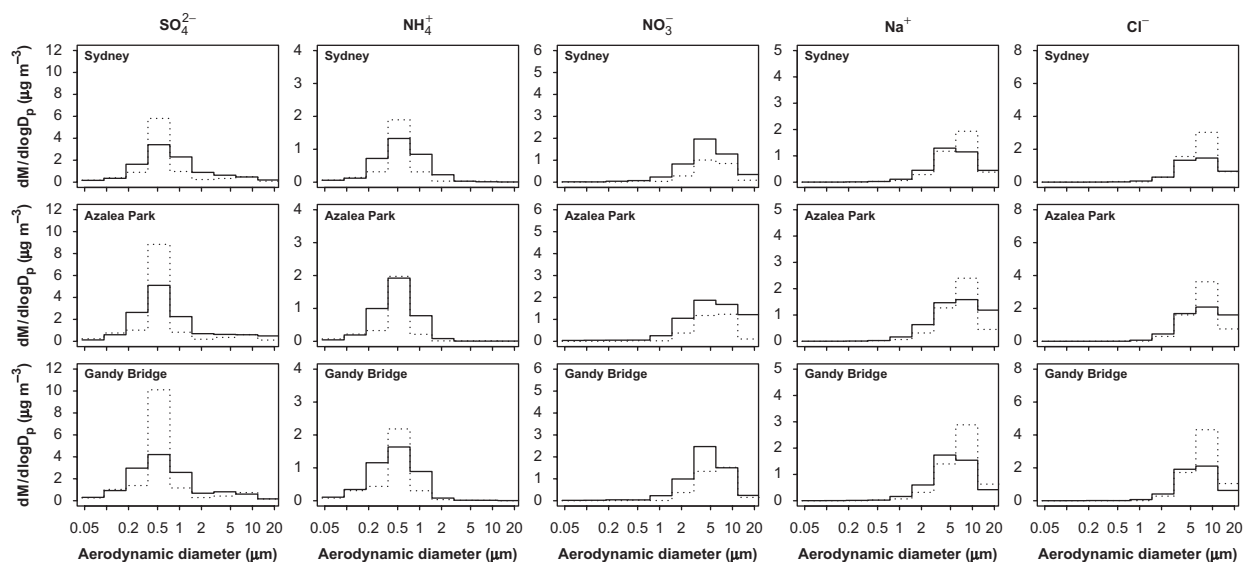


Fig. 3. Observed (solid) and model-predicted (dotted) size distributions of inorganic aerosol components at three Tampa-area sites averaged over 15 sampling days (14 at Sydney) during May 2002.

averaged over all sampling days in Fig. 3. Comparisons of day-specific observations and model predictions are available in the supporting material. At all three sites, predicted maxima in the size distributions are correct to within one size bin nearly every day for all chemical species. One noteworthy aspect that warrants further exploration is that predicted sulfate and ammonium peaks are too sharp, with overpredictions in the 4th size bin (0.31–0.63 μm) and underpredictions in bins 3 and 5. As noted previously, NO_3^- is consistently underpredicted by about a factor of two. However, CMAQ-UCD correctly identifies that aerosol NO_3^- was predominantly in coarse particles, a result which would be unattainable with the current version of CMAQ, in which interaction between the coarse mode and the gas phase is not simulated.

There have been relatively few comparisons of modeled aerosol size distributions against chemically speciated and size segregated measurements reported in the literature, and those comparisons that do exist are typically restricted to a few samples. Several studies have been conducted in which impactor measurements collected in southern California are compared to predicted size-composition distributions using both Lagrangian (Eldering and Cass, 1996; Kleeman et al., 1997) and Eulerian models (Meng et al., 1998; Sun and Wexler, 1998b; Kleeman and Cass, 2001; Moya et al., 2002). Los Angeles pollutant concentrations reported in these studies were much higher than measured in Tampa

during BRACE. Meng et al. (1998) were able to simulate the submicron mode of aerosol nitrate and ammonium very accurately, but missed the supermicron nitrate mode. They attributed this to the fact that coarse particle Na^+ and Cl^- were greatly underpredicted due to inaccuracies in their crude (uniformly distributed in space and time) sea-salt emission inventory. Sun and Wexler (1998b) used the same sea-salt emission inventory and also underpredicted coarse mode nitrate. Spyridaki et al. (2006) simulated aerosol dynamics in the eastern Mediterranean in both July 2000 and January 2001. They obtained excellent agreement in representing the size distribution of sulfate, ammonium, and nitrate, particularly for the winter case, but underpredicted the mass of all components (except crustal oxides) during the summer. Taken as a whole, the level of agreement exhibited in Fig. 3 and in the supporting information between the modeled and observed size distributions is as good, if not better, than previous attempts to simulate size-resolved inorganic chemical composition across fine and coarse particles.

4.3. Predicted and measured temporal patterns

The availability of continuous measurements of SO_4^{2-} , NH_4^+ , NO_3^- , Cl^- , and HNO_3 at Sydney provide a rare opportunity to test the modeled diurnal patterns of these species over an extended time period (1 May–2 June). Aerosol SO_4^{2-} , NH_4^+ ,

NO_3^- , and Cl^- time series plots are available in the supporting material. A close inspection of those plots yields the same conclusions drawn above based on the MOUDI data, with SO_4^{2-} essentially unbiased, NH_4^+ exhibiting a small negative bias, and NO_3^- exhibiting a larger negative bias. Additionally, the model frequently predicts large Cl^- peaks during the early morning hours which are not seen in the observations. Daytime predictions, however, are closer to observed values.

One possible cause of predicting too little aerosol nitrate is the underprediction of gas-phase nitric acid. One formation pathway for nitric acid is the nighttime heterogeneous reaction $\text{N}_2\text{O}_5 + \text{H}_2\text{O} \rightarrow 2\text{HNO}_3$. However, this pathway is not treated in the current formulation of CMAQ-UCD. To assess the importance of this reaction, sensitivity runs were conducted for the same time period. One sensitivity used the base CMAQ aerosol model, which includes heterogeneous conversion of N_2O_5 to HNO_3 , while in the other this reaction rate was set to 0. The mean difference in predicted total nitrate was $0.3 \mu\text{g m}^{-3}$, or about 10%.

The nitric acid time series at Sydney is shown in Fig. 4. The model accurately produces the timing of

many of the peaks seen in the observations, with occasional large overpredictions (e.g., 4, 5, 8, 13, and 15 May). Though there are periods when nitric acid is underpredicted (e.g., 20–23 May), the $1.62 \mu\text{g m}^{-3}$ average nitric acid concentration predicted by the model is in excellent agreement with the $1.51 \mu\text{g m}^{-3}$ average measurement. Therefore, the data indicate that the overall factor of two underprediction of aerosol nitrate is not primarily due to an underprediction of nitric acid.

There remains the possibility that inaccurate (or too slow) gas-to-particle conversion accounts for the underprediction of aerosol nitrate. Fig. 5 shows the aerosol fraction of total nitrate (NO_3^- aerosol + HNO_3). Averaged over the entire period, the observed aerosol nitrate fraction is 52%, only slightly higher than the model's 45% nitrate fraction. The amplitude of the aerosol fraction in the model is quite large, however, frequently reaching a minimum around 10% in the afternoon when temperatures are highest and peaking around 90% after midnight on 24–28 May. In contrast, the observations show a much narrower variation in the aerosol nitrate fraction. For 80% of the available observations, the fraction of total nitrate in the

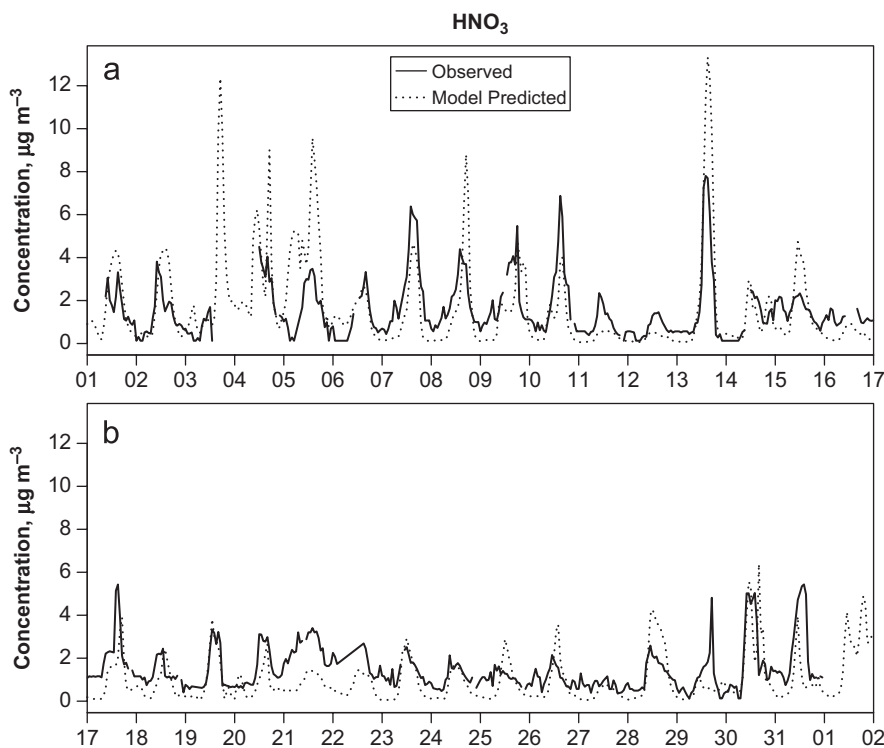


Fig. 4. Time series of observed and modeled nitric acid concentrations at Sydney, Florida, from 1 May to 2 June 2002. Tick marks represent 0000 local standard time for each day.

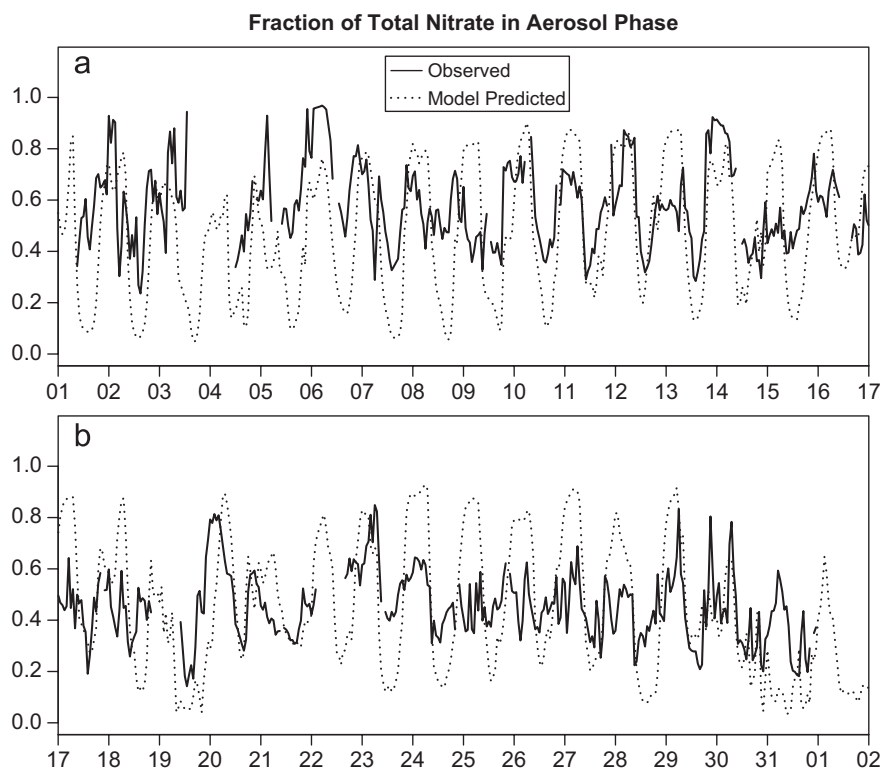


Fig. 5. Time series of observed and modeled fraction of total nitrate ($\text{HNO}_3 + \text{NO}_3^-$) present in the aerosol phase at Sydney, Florida, from 1 May to 2 June 2002. Tick marks represent 0000 local standard time for each day.

aerosol phase was between 30% and 70%, while the modeled aerosol nitrate fraction was in that range only 42% of the time.

4.4. Chloride depletion due to nitrate displacement

Average chloride to sodium molar ratios are plotted in the left column of Fig. 6. For all sizes greater than about $0.3 \mu\text{m}$, the observed chloride to sodium ratio is less than 1.17, their relative abundance in seawater (Stumm and Morgan, 1981). The deficit in the Cl^-/Na^+ ratio from 1.17 is a measure of the degree to which chloride has been depleted due to displacement by condensation of other acidic gases. This deficit reaches a maximum in the smallest size sections shown in Fig. 6, consistent with previous studies (Eldering et al., 1991; Pakkanen, 1996; Yao et al., 2003). The observed Cl^-/Na^+ ratio frequently increases for particles smaller than $0.3 \mu\text{m}$, and in some cases exceeds the ratio in seawater. This is likely due to condensation of NH_4Cl or other directly emitted sources of Cl^- (e.g., combustion). We exclude the

three smallest size bins in Fig. 6 because the absolute amounts are very small and because non-sea-salt sources of Na^+ and Cl^- that are not in the model may be important in determining fine aerosol concentrations. For particles larger than $1.3 \mu\text{m}$, the model captures the trend of increasing Cl^-/Na^+ with increased diameter, though it consistently overpredicts the Cl^-/Na^+ ratio. The nitrate to sodium molar ratios in the right column of Fig. 6 show that higher coarse particle nitrate is associated with decreased levels of chloride.

Continuous measurements of particulate Na^+ were not collected, so a surrogate measure of chloride depletion is derived from the continuous data. The MOUDI data (Fig. 3) indicate that there is very little fine particle nitrate at Sydney. Accordingly, the nitrate measured by the soluble particle collector is predominantly in coarse particles ($>1 \mu\text{m}$). With coarse particle nitrate emissions not expected to be significant, we can conclude that the NO_3^- that is present in the aerosol is due to heterogeneous reaction of HNO_3 with sea-salt particles. Accordingly, the molar sum of NO_3^- and

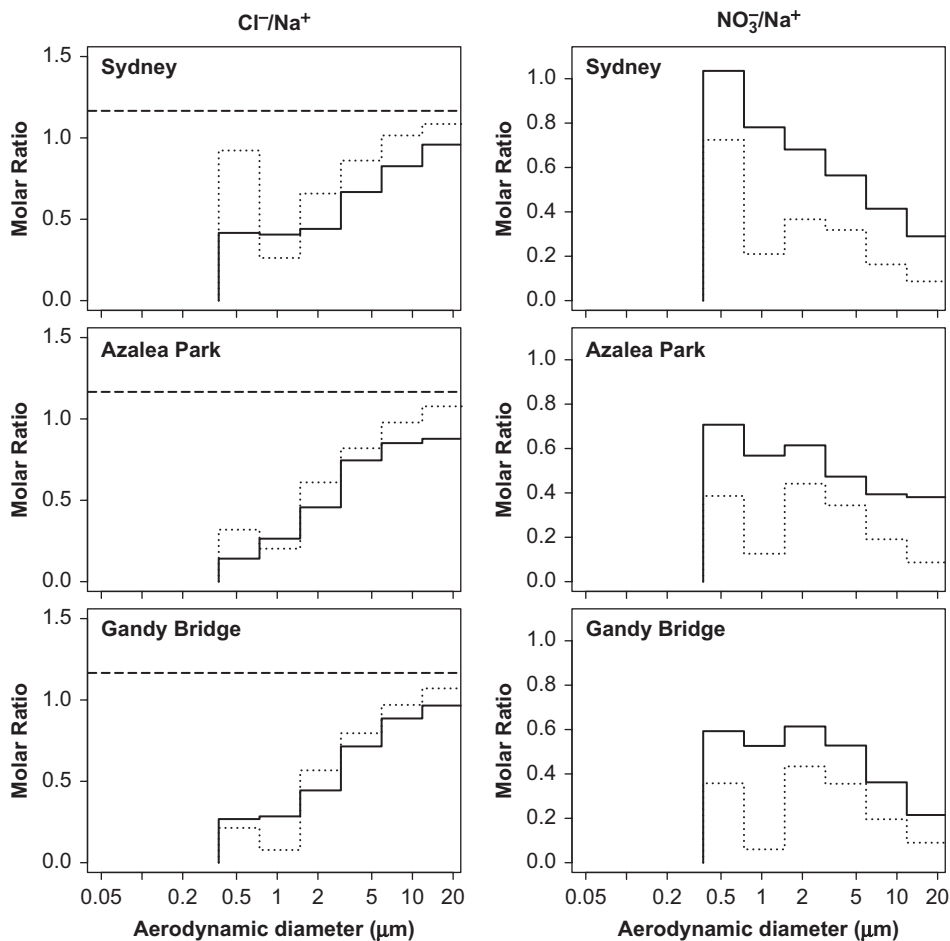


Fig. 6. Observed (solid) and model predicted (dotted) molar ratio of chloride and nitrate to sodium at three Tampa-area sites, averaged over 15 sampling days (14 at Sydney) during May 2002. The dashed line at 1.17 represents the average Cl^-/Na^+ ratio in seawater.

Cl^- can be used to approximate the semi-volatile anions in sea-salt aerosol, and the molar ratio of NO_3^- to the sum of NO_3^- and Cl^- indicates the degree of displacement of Cl^- by NO_3^- . This ratio (Fig. 7) frequently peaks at 6 p.m. in the observations, often indicating near 100% depletion (e.g., 7, 8, and 14 May). Though the modeled diurnal profile agrees well with the observations, peaking at the right times on 5, 7, 8, 13, 14, and 20 May, in each of these cases the model significantly underpredicts the extent of Cl^- depletion, with peak observed ratios exceeding 0.9 where the model peaks in the range 0.4–0.8. The average observed Cl^- depletion is 48%, while the average model predicted Cl^- depletion is 26%. However, on 30–31 May the model correctly displaced nearly 100% of the Cl^- from sea-salt particles, matching the observed ratios of >95%. This comparison with highly time-resolved measurements is in good agreement with the long-term

average result in the right column of Fig. 6, showing that model predictions of the ratio of coarse $\text{NO}_3^-/\text{Na}^+$ are too low. In combination, Figs. 6 and 7 suggest that the model underpredictions of NO_3^- are due in large part to insufficient displacement of Cl^- from sea-salt particles.

4.5. Model timing

With 12 aerosol components in each size section, CMAQ-UCD is computationally intensive compared to CMAQ, and as a consequence runs about 8–10 times slower. This computational expense may be unwarranted for standard regulatory applications, in which modeling $\text{PM}_{2.5}$ concentrations is the primary goal. At coastal urban locations such as Tampa, however, coarse sea-salt particles can be an important sink for nitric acid. A dynamic model

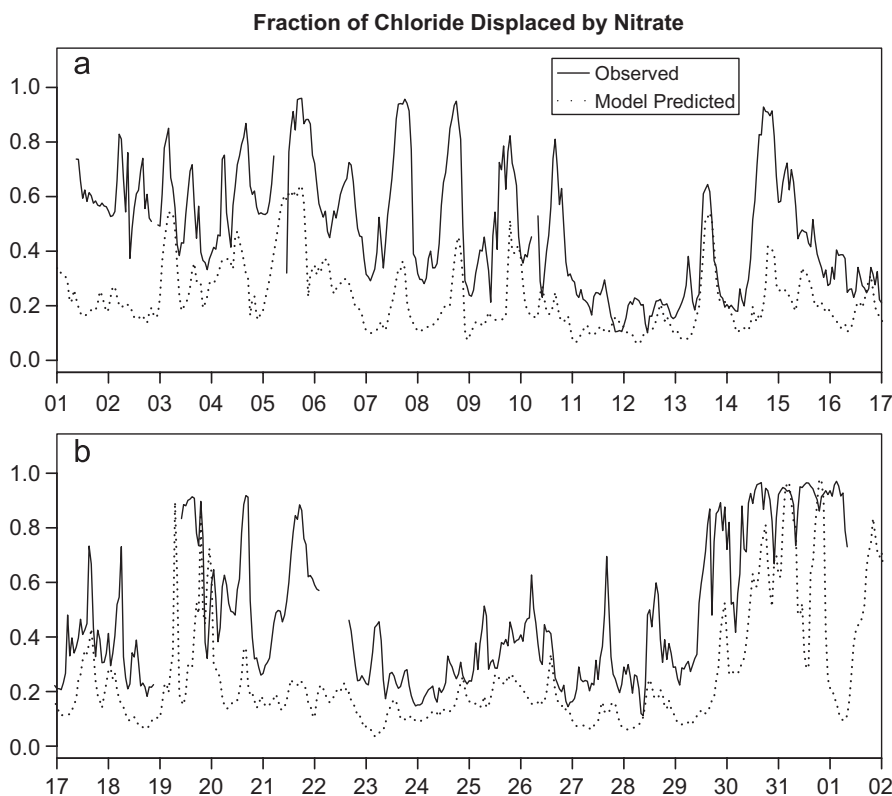


Fig. 7. Time series of observed and modeled chloride displacement by aerosol nitrate at Sydney, Florida, from 1 May to 2 June 2002. Tick marks represent 0000 local standard time for each day.

such as CMAQ-UCD and accurate emissions of sea salt are both necessary to represent this process.

5. Conclusions

The UCD sectional aerosol module has been coupled to CMAQ and applied to simulate PM concentrations at Tampa, Florida, a coastal urban site. Observations conducted during the BRACE field experiment constitute an especially rich data set against which to evaluate the model. Predicted 23-h sodium and chloride concentrations are relatively unbiased, indicating that the generation of sea-salt particles and their transport to the observational sites are correct on average. Average modeled inorganic aerosol size distributions are in excellent agreement with observations. Across the three sites and five species for which data are available for comparison, the model correctly predicts the size bin in which the peak occurs 87% of the time. However, predicted SO_4^{2-} and NH_4^+ peaks are too sharp, with the model overpredicting the peak in the $0.31\text{--}0.63\ \mu\text{m}$ size section and

underpredicting the amounts in the two adjacent sections. Though the model does correctly predict that nitrate is predominantly in coarse particles, modeled nitrate concentrations are biased low by a factor of two. Nevertheless, the level of agreement between the modeled and observed size distributions is as good, if not better, than previous attempts to simulate size-resolved chemical composition across fine and coarse particles.

The semi-continuous measurements of chemically speciated aerosol and gas-phase nitric acid facilitates evaluation of the model's treatment of gas-to-particle conversion. Though the modeled fraction of total nitrate in the aerosol phase is very close to the observed value on average, time series analysis shows that the variation of this fraction is much greater in the model than in the data. Averaged over the entire month, the modeled chloride depletion is 26%, significantly less than the 48% inferred from the observations. In addition, the relative abundances of Cl^- and NO_3^- to Na^+ allow the determination of coarse particle chloride depletion as a function of particle size. To our knowledge, this represents the

first evaluation of size-resolved mass transfer between gas-phase HNO_3 and HCl and coarse particle NO_3^- and Cl^- within a chemical transport model.

The frequent overpredictions in early morning chloride concentrations and the underprediction of the extent of chloride replacement by nitrate could be due to an underestimation of the rate of mass transfer to coarse particles, possibly driven by inaccurate thermodynamics. As noted by Moya et al. (2002), the crustal species Ca^{2+} , Mg^{2+} , and K^+ can have important effects on the partitioning of total nitrate, and their absence in the model may account for some of the observed discrepancies. Alternatively, the nitric acid and aerosol nitrate wet and dry deposition sinks may have been overestimated. Future work should explore the sensitivity of modeled aerosol nitrate concentrations on parameters such as the accommodation coefficient and the gas-phase diffusivity, as well as errors in modeled meteorological variables such as relative humidity. It would also be useful to apply the CMAQ-UCD model to a deposition field campaign.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.atmosenv.2007.12.059.

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