Atmospheric Environment 42 (2008) 6057–6066

Contents lists available at ScienceDirect

Atmospheric Environment

journal homepage: www.elsevier.com/locate/atmosenv

Evaluation of the community multiscale air quality (CMAQ) model version 4.5: Sensitivities impacting model performance; Part II—particulate matter

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ARTICLE INFO

Article history:
Received 14 August 2007
Received in revised form
19 March 2008
Accepted 20 March 2008

Keywords:
Community multiscale air quality (CMAQ) model
Model evaluation
$PM_{2.5}$
Sulfate
Nitrate
Ammonium
Organic and elemental carbon

ABSTRACT

This paper is Part II in a pair of papers that examines the results of the Community Multiscale Air Quality (CMAQ) model version 4.5 (v4.5) and discusses the potential explanations for the model performance characteristics seen. The focus of this paper is on fine particulate matter ($PM_{2.5}$) and its chemical composition. Improvements made to the dry deposition velocity and cloud treatment in CMAQ v4.5 addressing compensating errors in 36-km simulations improved particulate sulfate (SO_4^{2-}) predictions. Large overpredictions of particulate nitrate (NO_3^-) and ammonium (NH_4^+) in the fall are likely due to a gross overestimation of seasonal ammonia (NH_3) emissions. Carbonaceous aerosol concentrations are substantially underpredicted during the late spring and summer months, most likely due, in part, to a lack of some secondary organic aerosol (SOA) formation pathways in the model. Comparisons of CMAQ $PM_{2.5}$ predictions with observed $PM_{2.5}$ mass show mixed seasonal performance. Spring and summer show the best overall performance, while performance in the winter and fall is relatively poor, with significant overpredictions of total $PM_{2.5}$ mass in those seasons. The model biases in $PM_{2.5}$ mass cannot be explained by summing the model biases for the major inorganic ions plus carbon. Errors in the prediction of other unspeciated $PM_{2.5}$ (PM_{Other}) are largely to blame for the errors in total $PM_{2.5}$ mass predictions, and efforts are underway to identify the cause of these errors.

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1. Introduction

This paper is Part II in a pair of papers that present an operational evaluation of the Community Multiscale Air Quality (CMAQ) model version 4.5 (v4.5) that was released in 2005, with the focus of this paper on model performance for particles with aerodynamic diameter $<2.5\,\mu m$ ($PM_{2.5}$). The CMAQ v4.5 results presented here are from an annual 12-km CMAQ simulation for the eastern United States. Additional results can be found at http://www.cmaq-model.org, where the CMAQ model source code can be downloaded. Here, the emphasis will be to present key results that identify performance strengths, as well as problems warranting further investigation.

2. Description of CMAQ simulations

In this study, an annual (2001) CMAQ v4.5 simulation utilizing the CB-IV gas-phase chemistry mechanism (Gery et al., 1989) was developed with 12 km × 12 km horizontal grid spacing and a 14-layer vertical structure for the domain covering the eastern United States. The 12-km simulations were nested within coarse-grid simulations

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1352-2310/$ - see front matter Published by Elsevier Ltd.
doi:10.1016/j.atmosenv.2008.03.036

(36 km × 36 km horizontal grid spacing covering the continental United States) that used the same model configurations as the nested simulation. Boundary conditions for the 36-km simulation were obtained from a global chemical transport model (GEOS-CHEM) (Bey et al., 2001). The meteorological fields were simulated at both 36 and 12 km (nested within the 36-km simulation) by MM5, the Fifth-Generation Pennsylvania State University/National Center for Atmospheric Research (NCAR) Mesoscale Model (Grell et al., 1994). The MM5 fields were processed for CMAQ using version 3.0 of the Meteorology-Chemistry Interface Program (MCIP) (Byun and Schere, 2006). Full details regarding the specific options and inputs used for the CMAQ simulations can be found in Part I (Appel et al., 2007) of this pair of papers which discusses the ozone performance for the same simulations.

3. Observational data sets

Model performance is evaluated here against atmospheric concentrations of nitric acid (HNO_3) and fine particulate sulfate (SO_4^{2-}), nitrate (NO_3^-), ammonium (NH_4^+), elemental carbon (EC), organic carbon (OC), total carbon (TC), and gravimetric mass ($PM_{2.5}$). For this evaluation, observed concentrations are obtained from the Speciation Trends Network (STN), the Interagency Monitoring of Protected Visual Environments (IMPROVE) network and the Clean Air Status and Trends Network (CASTNet). Some details regarding each of these networks are summarized in Eder and Yu (2006). Since there are no calibration standards and each monitoring network has its own sampling methodology and measurement frequency, the model results need to be evaluated separately against each network (Gégo et al., 2005). Additionally, observed data contain uncertainties; however, these uncertainties are beyond the scope of this study. Here, observed data are compared with model results to evaluate model performance. Where systematic measurement errors are known to be present (e.g. CASTNet NO_3^- measurements), these comparisons are either not included or are limited to help account for the uncertainty in the observations.

In addition to the information provided in Eder and Yu (2006) for the STN, it is important to note that while the STN sampling procedure was developed to closely follow that of the IMPROVE network (Malm et al., 2004), the networks use different thermal optical protocols to quantify EC and OC. Chow et al. (2001) describe the differences between the IMPROVE thermal optical reflectance (TOR) protocol and the National Institute of Occupational Safety and Health (NIOSH) protocol which is used by the STN. They found that NIOSH EC was typically less than half of IMPROVE EC; however, IMPROVE and NIOSH TC values are in a good agreement with each other. For the purposes of the evaluation presented here, no attempt was made to apply any generalized correction to EC or OC measurements from either the STN or IMPROVE network.

Most of the EC and OC emission inputs to the present CMAQ simulations were computed using speciation profiles based on the IMPROVE TOR protocol, so a direct comparison of observations of EC and OC from the IMPROVE network to simulated concentrations of EC and OC from the CMAQ model is appropriate. However, the same direct comparison of simulated EC and OC concentrations to observed concentrations from the STN is not reported here because the speciation profiles are inconsistent with STN ambient measurements. Therefore, comparisons with the IMPROVE network will include EC, OC and TC, while comparisons with the STN will only include TC. Comparisons of the TC model predictions against STN will provide useful information about the model predictions of the total carbon budget in urban areas. It is important to note that observations of TC from the STN have been blank corrected for positive adsorption artifacts using network-wide, sampler-specific values (Frank, 2006).

4. Paired analysis methods employed

It is necessary for the CMAQ output to be post-processed for comparability with each observation network and species. First, a post-processing program is used to convert raw model variables into the quantities measured at the various networks. A list of CMAQ aerosol module variables can be found in Table 1 of Binkowski and Roselle (2003) and the sea-salt species have been updated in CMAQv4.5 as described by Shankar et al. (2005). From these variables, fine-particle SO_4^{2-}, NH_4^+, NO_3^-, and EC are approximated by summing the appropriate Aitken- and accumulation-mode concentrations. Fine-particle OC is estimated by summing the modeled concentrations of primary organic aerosol (POA), anthropogenic secondary organic aerosol (SOA), and biogenic SOA, in the Aitken and accumulation modes, using species-specific weighting factors as shown in

$$\mathrm{OC} = \frac{1}{1.2}\mathrm{POA} + \frac{90}{150}\mathrm{SOA_{anth}} + \frac{120}{177}\mathrm{SOA_{biog}} \quad (1)$$

Division of the modeled POA concentration by 1.2 removes the non-carbon organic mass (OM) that is assumed implicitly in the $PM_{2.5}$ speciation profiles used with the 2001 national emission inventory (NEI) (Bhave et al., 2007). The multiplicative factors applied to each SOA term in Eq. (1) correspond to the representative carbon masses in the aromatic (7.5 carbon atoms) and biogenic SOA precursors (10 carbon atoms) in CMAQ, and molecular weights assumed in the CMAQ model code for SOA_{anth} (150 g mol^{-1}) and SOA_{biog} (177 g mol^{-1}). Fine-particle mass is approximated by summing the modeled concentrations of all Aitken- and accumulation-mode species except water, as shown in

$$\mathrm{PM_{2.5}} = \mathrm{SO_4} + \mathrm{NO_3} + \mathrm{NH_4} + \frac{1.4}{1.2}\mathrm{POA} + \mathrm{SOA_{anth}} + \mathrm{SOA_{biog}} + \mathrm{EC} + \mathrm{Na} + \mathrm{Cl} + \text{Unspeciated Mass} \quad (2)$$

To approximate the oxidation of primary OM that is believed to occur during atmospheric transport, the modeled POA is scaled up in Eq. (2) such that the resulting POA has an OM/OC ratio of 1.4, which is considered the lowest reasonable estimate for atmospheric OM (Turpin and Lim, 2001). This factor is applied during

post-processing because POA oxidation is not treated in the CMAQ model. After the raw model variables have been post-processed in the above manner, a second post-processing program was used to pair observations and model results in space (no spatial interpolation) and time (daily or weekly depending on the network).

A variety of statistical metrics are used here to compare the observed and predicted concentrations. The median bias (MdnB) and normalized median bias (NMdnB) are used as measures of model bias. The median error (MdnE), root mean square error (RMSE) and normalized median error (NMdnE) are used as measures of model error. NMdnB and NMdnE provide normalized (%) measures of performance, while RMSE, MdnB and MdnE provide absolute ($\mu g\,m^{-3}$) measures of performance. The MdnB, MdnE, NMdnB and NMdnE are defined below as

$$\mathrm{MdnB} = \mathrm{median}(C_M - C_O)_N \quad (3)$$

$$\mathrm{MdnE} = \mathrm{median}|C_M - C_O|_N \quad (4)$$

$$\mathrm{NMdnB} = \frac{\mathrm{median}(C_M - C_O)_N}{\mathrm{median}(C_O)_N} \times 100\% \quad (5)$$

$$\mathrm{NMdnE} = \frac{\mathrm{median}|C_M - C_O|_N}{\mathrm{median}(C_O)_N} \times 100\% \quad (6)$$

where C_M and C_O are modeled and observed concentrations, respectively, and N is the total number of model/ob pairs. Median is preferred here over mean since observed PM species are generally not normally distributed, and therefore median is a better measure of the central tendency of the distribution than the mean, as the mean will be influenced by a relatively small proportion of the large values (in the case of a right skewed distribution) or small values (left skewed) present in the distribution's tail. In the case where the species is normally distributed, the mean and median would be the same, so either metric would yield the same result.

Representativeness challenges continue to be present whenever gridded predictions from a deterministic model are compared to observed data at a point in time and space, as deterministic models calculate the average outcome over a grid for a given set of conditions, while the stochastic component (e.g. sub-grid variations) embedded in the observations is not accounted for. These issues are somewhat mitigated for the comparisons made here, since observations from the STN and IMPROVE network are daily averages, while the CASTNet observations are weekly averages and mostly measuring secondary products. The longer temporal averaging helps reduce the impact of stochastic processes, which can have a large impact on shorter (e.g. hourly) periods of observation.

5. Results

The EPA has developed National Ambient Air Quality Standards for $PM_{2.5}$, and has recently designated 39 "non-attainment" areas across the United States that do not meet these standards (http://www.epa.gov/air/oaqps/greenbk/qindex.html). Current regulatory emission controls for $PM_{2.5}$ focus on the reduction of NO_x and SO_2 emissions, and therefore primarily on reduction of inorganic aerosols. After reductions in inorganic aerosols are considered in the Clean Air Interstate Rule (http://www.epa.gov/CAIR/), focus on residual non-attainment areas will then look at reducing organic aerosols and their emissions sources. It is important for these reasons to assess the model's ability to simulate the chemical composition of $PM_{2.5}$, not just its total concentration.

5.1. Sulfate (SO_4^{2-})

Particulate SO_4^{2-}, which is one of the largest contributors to total $PM_{2.5}$ mass in the eastern United States, especially during the warm months, has historically been simulated well by the CMAQ model (Mebust et al., 2003; Eder and Yu, 2006; Tesche et al., 2006). Simulations using CMAQ v4.4 with similar configurations as the v4.5 simulations were conducted for the winter (December, January and February) and summer (June, July and August) time periods at both 36- and 12-km horizontal grid spacing. The CMAQ v4.4 simulations showed a good performance for SO_4^{2-} at the 36-km grid spacing for the summer (Fig. 1a); however, a substantial overprediction of SO_4^{2-} was found with 12-km grid spacing (Fig. 1b). In these MM5 simulations, precipitation was overpredicted during the summer at the 36-km grid spacing, while at the 12-km grid spacing the precipitation performance was nearly unbiased. The improved precipitation predictions in the 12-km simulation revealed an overprediction of SO_4^{2-} that was previously masked by the overprediction of precipitation (which resulted in greater wash-out of particulate SO_4^{2-}) in the 36-km simulation.

Based on the analysis above, several changes were made to the CMAQ v4.5 code to improve the prediction of SO_4^{2-}. In the CMAQ model convective cloud module, the analytical mixing scheme was replaced with a new mixing scheme based on the asymmetric convective model (ACM) that was originally developed for planetary boundary layer (PBL) mixing (Pleim and Chang, 1992). The ACM simulates a detraining convective plume by non-local transport from the source layer directly to each model layer within the convective cloud. An important difference from the previously used regional acid deposition model's (RADM's) convective cloud model is that downward mixing in ACM is by gradual layer-by-layer compensatory subsidence. The RADM-cloud scheme restricts cloud coverage whenever the modeled mass flux over the 1 h time step exceeds the available below-cloud mass. This artificial restriction of cloud coverage is eliminated in the ACM-cloud scheme by setting a mixing time step according to mass flux constraints and iterating up to the lifetime of the cloud (1 h). Additionally, the ACM sets the maximum spatial coverage for non-precipitating clouds within a grid cell at 50% versus 90% for the RADM cloud scheme, which results in less aqueous production of SO_4^{2-} as compared to RADM.

There were also changes made to the aerosol dry deposition velocity in CMAQ, which affected $PM_{2.5}$ predictions (including SO_4^{2-}). These include a new form of the impaction term, restoration of the impaction process to

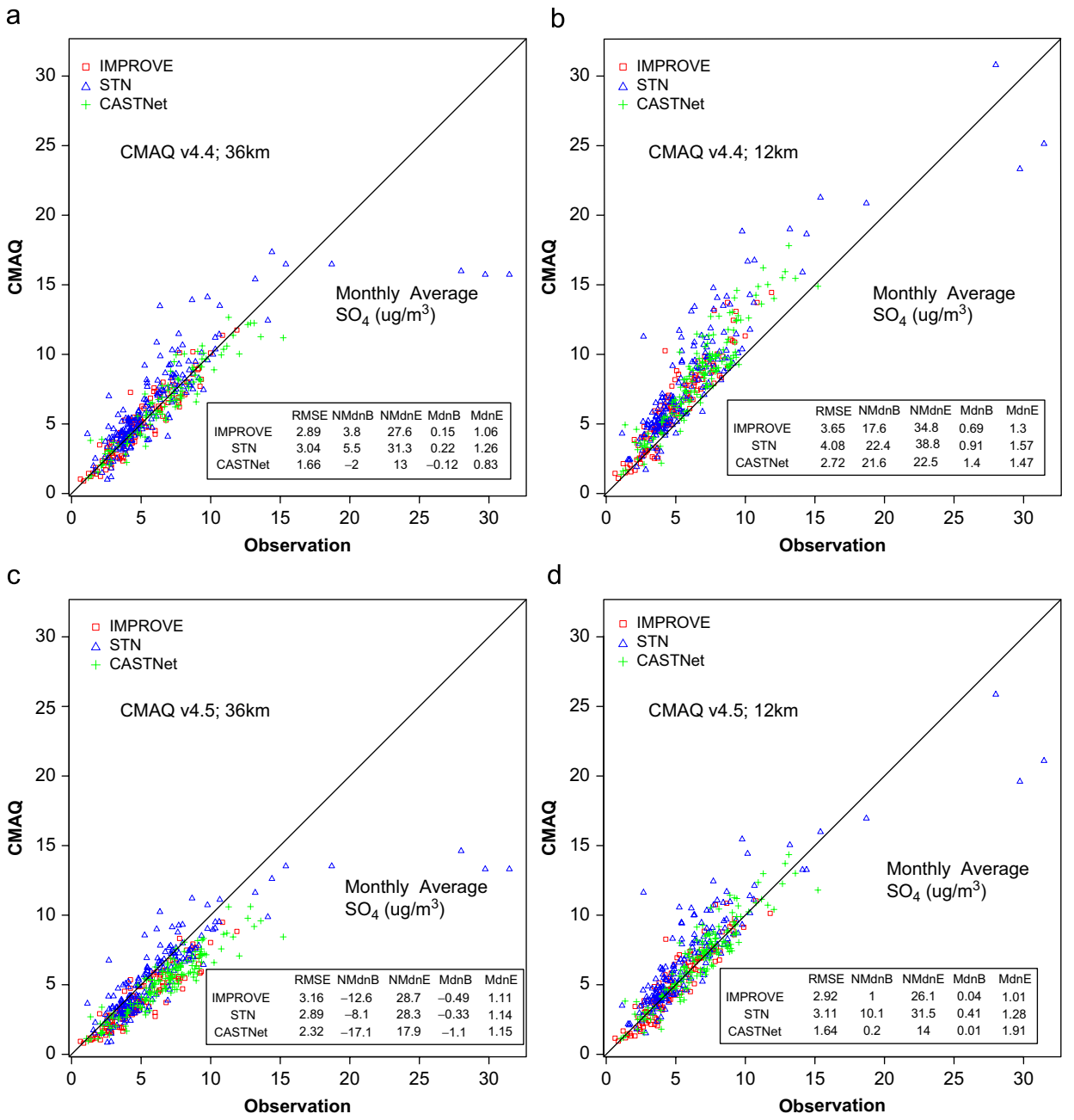

Fig. 1. Scatter plots (with 1:1 line) of monthly average SO_4^{2-} for the summer (June, July and August) 2001 for IMPROVE (red square), STN (blue triangle) and CASTNet (green cross) for (a) CMAQ v4.4, 36-km horizontal grid spacing (b) CMAQ v4.4, 12-km horizontal grid spacing (c) CMAQ v4.5, 36-km horizontal grid spacing and (d) CMAQ v4.5, 12-km horizontal grid spacing. Also shown are summary statistics of RMSE, normalized median bias (NMdnB; %), normalized median error (NMdnE; %), median bias (MdnB; $\mu g\,m^{-3}$) and median error (MdnE; $\mu g\,m^{-3}$) for each network.

coarse mode and the replacement of the equation for combining turbulent deposition fluxes and gravitational settling. The original form of the impaction term was observed to change too abruptly as aerosol size decreases, resulting in dry deposition velocities in the accumulation mode that are too small. The new form of the equation is based on a form of the impaction term suggested by Giorgi (1986). Using this new modally integrated impaction term, deposition velocities are greater in the accumulation mode. Additionally, the dry deposition velocity equation was updated to the form suggested by Venkatram and Pleim (1999), resulting in a small difference in aerosol dry deposition velocities.

These changes in cloud treatment and aerosol dry deposition in CMAQ v4.5 improved the model performance of fine-particulate SO_4^{2-} at the 12-km grid spacing (cf. Fig. 1d and b). SO_4^{2-} performance at the 36-km grid spacing suffered slightly as a result of the changes, with NMdnB increasing

from nearly unbiased using CMAQ v4.4 to between −8% (STN) and −17% (CASTNet) for CMAQ v4.5. This increase in bias can be attributed largely to precipitation biases in the 36-km inputs discussed above. Fig. 2a and g shows the SO_4^{2-} monthly domain-wide MdnB and NMdnB, respectively, for the various networks for the 12-km simulation using CMAQ v4.5. SO_4^{2-} is underpredicted in the winter at the rural IMPROVE and CASTNet sites, and overpredicted in the fall, most notably at the urban STN sites. The bias is relatively small in the spring and summer.

These results are consistent with those of Tesche et al. (2006), who found that their CMAQ v4.4 simulation underpredicted particulate SO_4^{2-} in the winter and spring and overpredicted SO_4^{2-} in the summer and fall. Tesche et al. (2006) did note that their MM5 simulation had a positive wet bias during the spring, summer and fall, which may have been compensating for the errors in the cloud treatment and dry deposition in CMAQ v4.4. Eder and Yu (2006) found a larger underprediction of particulate SO_4^{2-} in the winter than shown here and nearly no bias in the summer, which is attributable to the changes made in the CMAQ model code that directly affected SO_4^{2-} predictions and the overprediction of precipitation in the 36-km meteorology. It is important to note that while Tesche et al. (2006) and Eder and Yu (2006) provide convenient references for the performance seen here, there are significant differences between the CMAQ simulations evaluated in each study that impact the results of the model performance. Aside from both studies using an older version of CMAQ (v4.4), Tesche et al. (2006) examined a simulation for a different year (2002) that used significantly different emissions and meteorology than were used in the current study, while Eder and Yu (2006) examined a simulation for the same year (2001) that used the same emissions and meteorology as were used here but presented performance results for the 36-km simulation.

5.2. Ammonium (NH_4^+)

Fig. 2b and h shows the monthly domain-wide MdnB and NMdnB for NH_4^+, respectively. Model performance for NH_4^+ is relatively good throughout the year, except for the fall, when a large overprediction is present. Overpredictions in fall have been attributed to biases in the seasonal distribution of the NH_3 emissions (Gilliland et al., 2006). While the NH_4^+ performance is similar to that found by Eder and Yu (2006), the results differ from those of Tesche et al. (2006), where they found a large overprediction of NH_4^+ from November through February and an underprediction in the summer (June–August) at the CASTNet sites. The likely reason for the difference is the use of different seasonal distributions of NH_3 emissions, as here NH_3 emissions were based on seasonal estimates from Gilliland et al. (2006).

5.3. Nitrate (NO_3^-)

Particulate NO_3^- is overpredicted across all networks in March, October and November and underpredicted in the summer (Fig. 2c and i). Diagnostic investigations by Yu et al. (2005) show that a large source of error in predicting aerosol NO_3 across the eastern United States stems from errors in the 3-D model predictions of NH_x (NH_4^++NH_3), SO_4^{2-}, and, to a lesser extent, TNO_3 (NO_3^-+HNO_3). Observations of NH_x are not available at routine monitoring sites, so that dependency is difficult to explore in the present study. However, the gross overestimation of NH_3 emissions in the fall months discussed above is indicative of NH_x overpredictions during that season. Excess quantities of NH_x in the CMAQ simulations lead to NO_3^- overpredictions in October and November (Fig. 2c and i). An example of the influence of SO_4^{2-} errors on NO_3^- performance can be seen in February and March (Fig. 2a and c) where underestimates of SO_4^{2-} result in excess NH_3 available for NO_3^- formation, which leads to NO_3^- overpredictions. As shown in Fig. 2d and j, TNO_3 is overpredicted during 9 out of 12 months across the CASTNet, most notably in June-December. Overpredictions of TNO_3 occur due to overestimated NH_3 emissions and higher values of the N_2O_5 uptake coefficient. Overpredictions of TNO_3 during October and November are partly a side effect of the overestimated NH_3 emissions, because the artificially enhanced NO_3^- concentrations are removed more slowly by dry deposition than HNO_3 (Dennis et al., 2008), while the overpredictions in February and March are likely due to the overprediction of NO_3^- formation via heterogeneous hydrolysis of N_2O_5. The cause of TNO_3 overpredictions from June through September is unclear.

5.4. Carbonaceous aerosols

Fig. 2e and k shows monthly domain-wide MdnB and NMdnB, respectivlely, of EC, OC and TC for the IMPROVE network sites and TC for the STN sites. EC and OC at the rural IMPROVE sites are underpredicted from May through August, although biases in EC are small due to the small absolute concentrations of EC (observed concentrations normally range between 0.15 and 0.55 $\mu g\,m^{-3}$ in the summer). Performance of TC at the urban STN sites is similar to that of TC at the IMPROVE network sites from March through November, with relatively large underpredictions (0.6–1.2 $\mu g\,m^{-3}$) for May through August. However, unlike the IMPROVE network, TC performance at the STN sites during the winter is poor, with relatively large overpredictions in January and February as compared to IMPROVE network sites. One contributing factor to the large bias in January and February may be increased variability in the observations during the instrument "burn-in" period as the STN was being established. Alternatively, this may be indicative of excessive emissions estimates from residential wood combustion in the NEI. Simulations performed for 2002 using CMAQ v4.6 and an updated version of the NEI show a similar pattern to the TC bias at STN sites but with much lower bias in winter, particularly in January and February.

The results from comparisons to the IMPROVE network sites are similar to Tesche et al. (2006), where they found EC and OC were underpredicted throughout the year, with the largest underpredictions occurring in the summer and

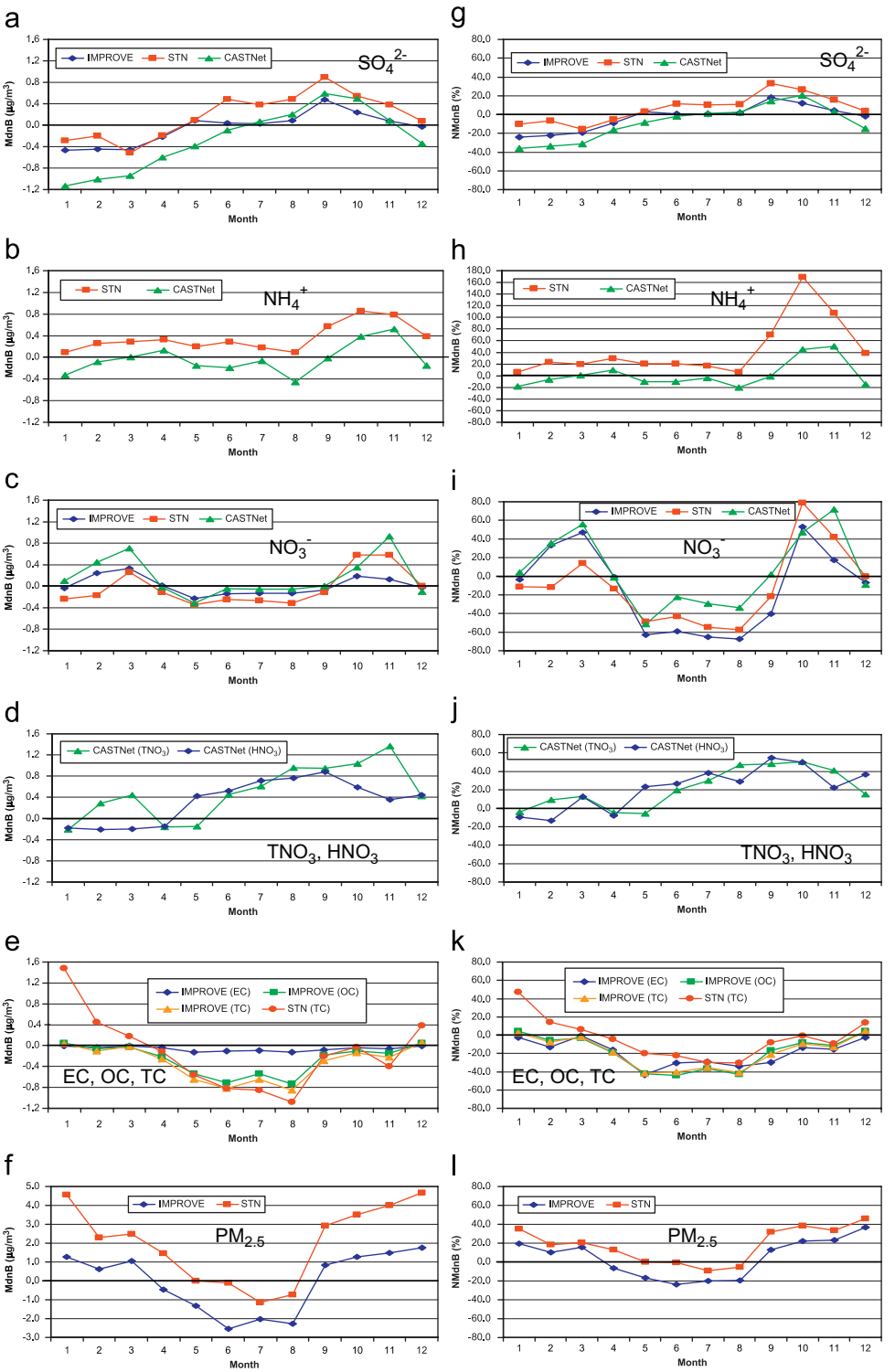

Fig. 2. Monthly (2001) average median bias (MdnB; $\mu g\,m^{-3}$) and normalized median bias (NMdnB; %) for CMAQ (v4.5 12-km) predicted (a) and (g) SO_4^{2-}; (b) and (h) NH_4^+; (c) and (i) NO_3^-; (d) and (j) CASTNet TNO_3 (green triangles) and HNO_3 (blue diamonds); (e) and (k) EC (blue diamonds), OC (green squares) and TC (yellow triangles for IMPROVE, red squares for STN); (f) and (l) $PM_{2.5}$. In figures (a), (b), (c), (f), (g), (h), (i) and (l), IMPROVE is shown as blue diamonds, STN is shown as red squares and CASTNet is shown as green triangles. Month is shown along the abscissa. MdnB ($\mu g\,m^{-3}$) is shown in figures (a) through (f), while NMdnB (%) is shown in figures (g) through (l).

fall. EC and OC performance for the CMAQ v4.5 36-km simulation (not shown) are notably different than the 12-km simulation. For the 36-km simulation, OC is overpredicted throughout the majority of the year, with the exception of June and November, when OC is underpredicted. EC tends to be slightly underpredicted throughout the majority of the year, except for January and August, when EC is largely overpredicted. The overprediction of EC in January and August is largely due to the overprediction of EC at sites in the west. When the analysis of the 36-km grid is limited to only the sites present in the 12-km domain, the overprediction in January and August largely disappears and the results become consistent with the 12-km grid results. Overall, the 36-km simulation results are consistent with the results of Eder and Yu (2006) for their CMAQ v4.4 36-km simulation.

A natural starting point for identifying potential causes of the seasonal biases in carbonaceous aerosol predictions is the emissions inventory. Since EC is commonly used as a tracer for carbon emitted from combustion sources, the underpredictions in EC suggest that the TC emission inventory is too low in the summer season. Bhave et al. (2007) found that modeled contributions of TC from vehicle exhaust and biomass combustion, the two largest sources of primary carbon, are unbiased across the southeastern United States during the summer. This implies that the summertime underpredictions of TC in the Southeast are not dominated by emission errors. Similar evaluations of the TC inventory in other parts of the eastern United States are warranted.

Another possible explanation for the underestimations of TC and OC during summer months is the likely underestimation of secondary organic aerosol (SOA) in the eastern United States. As discussed by Morris et al. (2006), the standard CMAQ model does not include SOA formation resulting from the oxidation of isoprene or sesquiterpenes, both of which may contribute substantial quantities to the ambient OC concentration in the eastern United States. Efforts are underway to implement these SOA formation pathways in the next version of CMAQ (Edney et al., 2007). Based on tests by Morris et al. (2006), including these SOA pathways could entirely mitigate the summertime underpredictions in OC across the east, though overpredictions in the west may be exacerbated.

5.5. Total $PM_{2.5}$ mass

On average, total $PM_{2.5}$ mass tends to be overpredicted in the fall and winter, underpredicted in the summer and relatively unbiased in the spring (Fig. 2f and l). The overprediction in the fall and winter is greatest at the urban STN sites; while the underprediction in the summer is greatest at the rural IMPROVE network sites. Note that in Fig. 2f the scale is much larger than for the other species, indicating that the bias in total $PM_{2.5}$ mass cannot be explained by summing the bias in the major inorganic and carbon species. Additionally, the correlation in bias throughout the year between the STN and IMPROVE network sites, with the STN bias consistently higher than the IMPROVE bias, indicates a systematic bias in the rural (IMPROVE) versus urban (STN) predictions. While the results of comparisons of $PM_{2.5}$ mass from the STN and IMPROVE network sites to predictions from the 36-km simulation (not shown) are consistent with the results of Eder and Yu (2006), they are notably different from the results from the 12-km simulation, where the bias at STN sites is much larger in the winter for the 12-km simulation than the 36-km simulation.

Fig. 4 shows seasonal stacked bar charts of STN observed total $PM_{2.5}$ mass and CMAQ predicted total $PM_{2.5}$ mass for four regions (Fig. 3), with each of the individual particulate species (SO_4^{2-}, NO_3^-, NH_4^+, TC and PM_{Other}) color coded to show its contribution to the total $PM_{2.5}$ mass concentration. The best agreement between predicted and observed total $PM_{2.5}$ mass is in the spring (Fig. 4a) and summer (Fig. 4b), when predicted values are generally within 2.0–4.0 $\mu g\,m^{-3}$ of the observations. Total $PM_{2.5}$ mass is underpredicted in the spring in the Atlantic and South regions, mostly due to underpredictions in TC and PM_{Other}. A slight overprediction in total $PM_{2.5}$ mass is noted in the northeast region in the spring, while there is a very good agreement between the observed and modeled species in the Great Lakes region. In the summer, total $PM_{2.5}$ mass is slightly overpredicted in the Great Lakes region and underpredicted in the other three regions. SO_4^{2-} is overpredicted in the summer in all regions, while NO_3^- and TC tend to be underpredicted for all the regions. PM_{Other} is overpredicted in the Great Lakes region and underpredicted to varying degrees in the other regions in the summer.

In the fall (Fig. 4c) and winter (Fig. 4d), total $PM_{2.5}$ mass is almost always overpredicted in all regions (the exception being the Atlantic region in the fall), with the best agreement to observed $PM_{2.5}$ mass in the Atlantic region, where the overprediction is $<3\,\mu g\,m^{-3}$. For the other regions, the overprediction is much larger, generally between 5 and 8 $\mu g\,m^{-3}$, and is dominated by overpredictions of PM_{Other}. Ignoring the contribution of

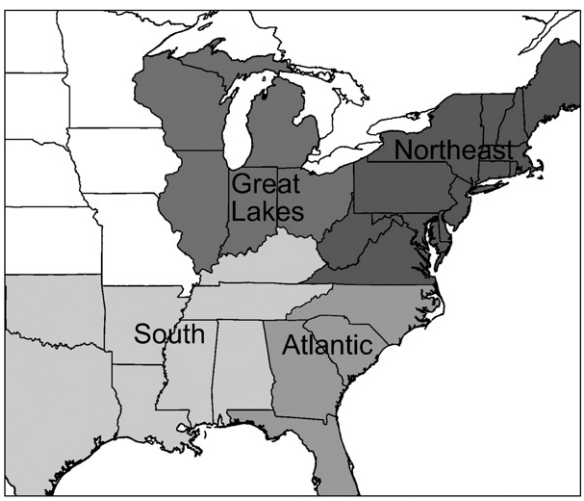

Fig. 3. States defining the regions for $PM_{2.5}$ analysis.

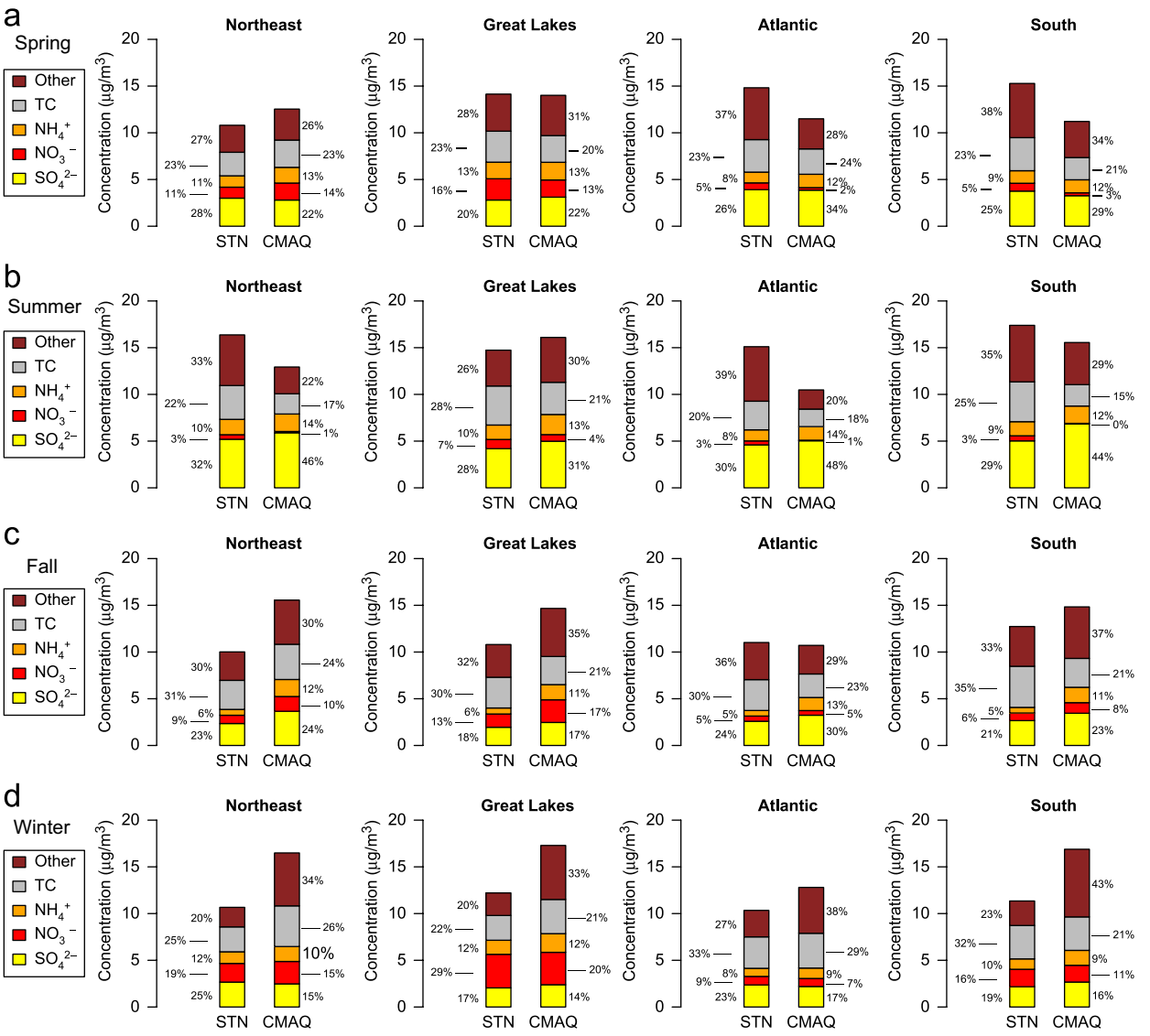

Fig. 4. Stacked bar charts of total $PM_{2.5}$ mass for the northeast, Great Lakes, Atlantic and South PCA regions (STN left, CMAQ v4.5 12-km right) for (a) spring (b) summer (c) fall and (d) winter. Concentration ($\mu g\,m^{-3}$) is shown along the abscissa. The individual aerosol species comprising the total $PM_{2.5}$ mass are shaded: SO_4^{2-} (sulfate; yellow); NO_3^- (nitrate; red); NH_4^+ (ammonium; orange); TC (total carbon; gray); PM_{Other} (brown). Included next to each species is the percent it contributes to the concentration of total $PM_{2.5}$ mass.

PM_{Other} to total $PM_{2.5}$ mass, the agreement between observed and predicted $PM_{2.5}$ mass would be considerably better, with predicted values within roughly $3\,\mu g\,m^{-3}$ of the observations for all regions. The large overprediction in PM_{Other} in the northeast and Great Lakes regions during the winter may be at least partially due to emissions of residential wood combustion that were too high in the emissions inventory. Corrections have since been made to the residential wood combustion in the NEI. Simulations using the corrected version of the NEI showed a small improvement in the PM_{Other} bias; however, large overpredictions in PM_{Other} in the northeast and Great Lakes regions during the winter and fall were still present.

5.6. PM_{Other}

The analysis above illustrates how PM_{Other} can make a significant contribution to total $PM_{2.5}$ mass. In the CMAQ output, PM_{Other} consists of the non-carbon atoms associated with OC as well as particulate emissions that are not explicitly speciated in the SMOKE processor, which includes trace elements (e.g. Fe, Si, K, etc.), primary NH_4^+ and other unidentified mass in the speciation profiles. The observed PM_{Other}, which is computed as the gravimetric mass minus the sum of TC, NH_4^+, NO_3^- and SO_4^{2-}, similarly contains trace elements, the non-carbonaceous portion of OC and some mass from water. In the winter and fall, the large overprediction in total $PM_{2.5}$ mass is largely driven

by the overprediction in PM_{Other}. Since the majority of predicted PM_{Other} from CMAQ consists of primary emissions, major biases are likely in some of the unspeciated primary emissions. Efforts are underway to subdivide the unspeciated emissions into trace elements using new speciation profiles available in the SPECIATE 4.0 database (Hsu et al., 2006). Once these emissions can be tracked in the CMAQ model, they can then be compared to observations of trace elements at the STN and IMPROVE network and any temporal biases in specific elements that contribute to the seasonal biases in PM_{Other} can be identified. Given its large contribution to total $PM_{2.5}$ mass, the PM_{Other} will be a focus of future diagnostic analyses.

Several other issues could be affecting the model performance as presented in the stacked bar charts. First, primary emissions of NH_4^+ are not speciated in SMOKE, and as a result CMAQ predictions of NH_4^+ contain only secondary NH_4^+, while primary emissions of NH_4^+ are lumped in the PM_{Other} category. Observed concentrations of NH_4^+ contain both primary and secondary contributions. Second, several studies (Chow et al., 2005; Hering and Cass, 1999) have shown losses of NO_3^- during and after sampling can be on the order of several micrograms during summer. Additionally, the predicted $PM_{2.5}$ mass does not include any contribution from water mass. While the STN filters are dried to remove the bulk of the water mass from the filter, there can be residual particle bound water that can positively bias the concentration of total $PM_{2.5}$ mass measured on the filter relative to a completely dried sample. Frank (2006) found that the monthly average concentration of STN water mass varied between approximately 0.5 and 3.0 $\mu g\,m^{-3}$ as a function of the monthly average concentration of the sum of the measured SO_4^{2-} and NH_4^+.

Finally, the STN uses a sharp cutoff at 2.5 μm to separate fine particles ($<2.5\,\mu m$) from the larger particles. CMAQ, however, outputs mass concentrations of the various PM species within three log-normal size distributions, referred to as modes (Binkowski and Roselle, 2003). While the first two modes, Aitken and accumulation, are typically summed together to estimate $PM_{2.5}$, the tail end of the accumulation mode can exceed the 2.5 μm cutoff. Using a method proposed by Jiang et al. (2006), a modified discrete cutoff was applied to the CMAQ model output to mimic the sharp cutoff of the observations. Efforts are underway to apply adjustments to the CMAQ predictions to account for the various issues discussed above and examine the impact the changes have on model performance results.

6. Summary

This paper examines the results of CMAQ version 4.5, utilizing model simulations at 36- and 12-km horizontal grid spacings. Several changes in CMAQ v4.5 affected the prediction of particulate SO_4^{2-}. Specifically, a new mixing scheme based on the ACM was introduced into the convective cloud module, along with the inclusion of a new calculation for aerosol dry deposition velocity. These changes resulted in an improvement in particulate SO_4^{2-} predictions over the previous version of the CMAQ model for the 12-km simulation, where modeled precipitation was nearly unbiased. Particulate SO_4^{2-} performance for the 36-km simulation is slightly degraded by the changes in CMAQ v4.5. However, this degradation in performance is related to a systematic overprediction of precipitation by MM5 for the 36-km horizontal grid spacing. The changes represent an improvement over the previous version of the model.

Performance for NH_4^+ was relatively good throughout the year, except in the fall where large overpredictions were observed, which are likely due to biases in the seasonal distribution of NH_3 in the emissions inventory. Particulate NO_3^- is overpredicted in the spring and fall and underpredicted in the summer. Recent diagnostic investigations by Yu et al. (2005) show that model performance for NO_3^- is strongly dependent on model performance for NH_x, SO_4^{2-}, and TNO_3. Excess quantities of NH_x in the CMAQ predictions in the fall lead to NO_3^- overpredictions.

Based on both IMPROVE and STN data, model predictions of carbonaceous aerosols show substantial underpredictions during the late spring and summer months. Some biases are suspected in the primary OC emissions during these time periods, and underpredictions in EC are most likely related to emission biases. Further work is essential to evaluate and refine the emission inventories for EC and primary OC. The standard CMAQ model does not include SOA formation resulting from the oxidation of isoprene or sesquiterpenes, both of which may contribute substantial quantities to the ambient OC concentration in the eastern United States. A new SOA mechanism will be incorporated into the next version of the CMAQ model, which may also improve model performance for OC and TC.

Comparisons of CMAQ total $PM_{2.5}$ mass predictions to observed $PM_{2.5}$ mass from the STN sites showed mixed seasonal performance. Spring and summer had the best overall performance, while the performance in the winter and fall was rather poor, with significant overpredictions of total $PM_{2.5}$ mass in those seasons. The largest contributor to the overpredictions in the winter and fall is from large overpredictions in PM_{Other} (unspeciated components of $PM_{2.5}$ mass). These results are consistent with those of Mathur et al. (2008), who found the operational version of the CMAQ model largely overpredicted PM_{Other} in the winter. It is likely that errors in the primary emissions that comprise the PM_{Other} are responsible for the majority of the bias. Several diagnostic evaluations are being performed to address the overpredictions in PM_{Other}, such as an effort to subdivide the primary unspeciated emissions in the CMAQ system that account for the bulk of the concentration of PM_{Other}, in order to identify specific trace elements that are responsible for the large differences in observations versus predictions seen in the PM_{Other} species. A correction to the residential wood combustion in the emissions inventory resulted in a small improvement in the PM_{Other} predictions; however, large overpredictions in PM_{Other} were still present in the fall and winter.

Acknowledgements

Thanks to Lucille Bender of Computer Sciences Corporation for helping run the model simulations. The research presented here was performed under the Memorandum of Understanding between the US Environmental Protection Agency (EPA) and the US Department of Commerce's National Oceanic and Atmospheric Administration (NOAA) and under agreement number DW13921548. This work constitutes a contribution to the NOAA Air Quality Program. Although it has been reviewed by EPA and NOAA and approved for publication, it does not necessarily reflect their policies or views.

Appendix A. Supplementary materials

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.atmosenv.2008.03.036.

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