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Model sensitivity evaluation for organic carbon using two multi-pollutant air quality models that simulate regional haze in the southeastern United States

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Abstract

Photochemical grid models are being used in technical analyses by the Visibility Improvement State and Tribal Association of the Southeast (VISTAS), a regional air quality planning organization in the southeastern United States, to support state implementation plans for regional haze and related air quality issues. VISTAS has embarked on a multi-phase process of testing and evaluating regional meteorological, emissions and air quality models that will be used to project visibility improvements as required by the regional haze rule. VISTAS has generated 2002 annual emissions and meteorological inputs for two photochemical grid models, the community multi-scale air quality (CMAQ) and the comprehensive air-quality model with extensions (CAMx), at a 36 km resolution for the continental US and at 12 km resolution for the eastern US. The two models were evaluated using speciated PM measurements from various monitoring networks and detailed analysis was performed for organic carbon (OC) mass using the IMPROVE, STN, and SEARCH networks. The differences in model performance between CMAQ and CAMx were used as a diagnostic tool to investigate performance issues for several compounds. CAMx performed substantially better than CMAQ for OC (defined as $1.4 \times$ measured organic carbon) which led to investigations into methods for improving the CMAQ OC model performance. The treatment of secondary organic aerosol (SOA) was identified as an area needing improvements in both models. The impact of replacing the CMAQ SOA parameters with those from CAMx was investigated. Further analysis identified several processes that are potentially important for SOA formation that are not treated in either model including, polymerization of the SOA into non-volatile particles and SOA formation from sesquiterpene, isoprene and other biogenic VOCs. A prototype mechanism for several of these missing processes was developed and the CMAQ SOA module was enhanced to include these SOA formation processes. SOA yields, specifically from biogenic emissions, were increased by

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the modified SOA module and CMAQ model performance for particulate OC at the IMPROVE, SEARCH, and STN sites in the VISTAS region was improved.

Keywords: Visibility; Fine particulate; Organic carbon; Secondary organic aerosol; CMAQ; CAMx

1. Introduction

The US Environmental Protection Agency (EPA) issued the regional haze rule (EPA, 1999a) to improve visibility in 156 designated Class I areas (national parks over 600 acres and wilderness areas over 5000 acres). The rule requires states to improve visibility on the haziest days and prevent degradation of visibility on the clearest days and to develop long-term strategies to reach natural background visibility conditions by 2064. States are required to submit State implementation plans (SIPs) by December 2007 that demonstrate reasonable progress in 2018 toward the visibility goals for each Class I area in their state. The Visibility Improvement State and Tribal Association of the Southeast (VISTAS) is a collaborative effort between ten states (AL, FL, GA, KY, MS, NC, SC, TN, VA, and WV), the eastern band of the Cherokee Indians, local air control agencies, EPA, federal land management agencies, and representatives from industry. VISTAS is conducting the technical analyses and planning activities necessary to support SIPs for regional haze and related air quality issues in the southeastern United States.

VISTAS has embarked on a multi-phase program to develop the regional meteorological, emissions and air quality modeling capability needed to simulate and project fine particulate matter, ozone and visibility in the southeastern US. Phase I of the VISTAS modeling included preliminary model testing to evaluate the capabilities of currently operational emissions, meteorological and PM/visibility models to define an optimal model configuration for annual modeling performed under phase II.

2. VISTAS phase II modeling approach

Phase II of the emissions and air quality modeling performed for VISTAS included annual modeling of the 2002 base year to develop a regional haze modeling database that can be used to project future-year visibility to demonstrate compliance with the regional haze rule. The phase II modeling is being conducted on both a 36 km resolution national US and 12 km resolution eastern US modeling domain. The MM5 meteorological model (Grell et al., 1994), the sparse matrix operator kernel emissions (SMOKE) emissions modeling system (Houyoux et al., 2000; UNC, 2004) and the Models-3 community multi-scale air quality (CMAQ) ozone/PM photochemical grid modeling system (Byun and Ching, 1999) were selected as the primary modeling tools for the VISTAS phase II modeling. The comprehensive air quality model with extensions (CAMx) ozone/PM model (ENVIRON, 2004) was also applied to corroborate the CMAQ results. These models and their configurations were selected after an extensive model sensitivity analysis of three episodes (January 2002, July 1999 and July 2001) conducted as part of the VISTAS phase I study (Olerud and Sims, 2003; ENVIRON et al., 2003a,b,c; Morris et al., 2004a).

The CMAQ and CAMx models were applied for 2002 on the 36/12 km grid and the model estimates for carbonaceous species were compared against speciated PM measurements from the IMPROVE (Malm et al., 2000), STN (EPA, 1999b) and SEARCH (Hansen, 2002) networks. The phase II modeling protocol details the procedures used in the 2002 annual modeling (ENVIRON et al., 2003d). Fig. 1 displays the 12 km eastern US modeling domain, the ten VISTAS states outlined in bold, and the locations of the monitors used in the OC model evaluation. Details on the operational model performance evaluation of the CMAQ and CAMx models across all PM species are provided in a companion paper to this one (Tesche et al., 2006) and in the project report (Morris et al., 2004b). Below we discuss the model performance evaluation of the CMAQ and CAMx models to investigate why the models exhibit poor organic carbon (OC) model performance and how the CMAQ model was enhanced to describe SOA formation processes that were not previously accounted for in the model with subsequent improved performance.

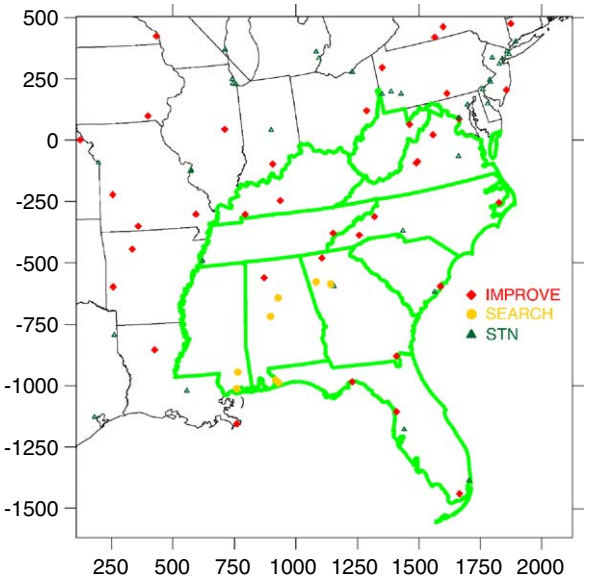

Fig. 1. Location of IMPROVE, SEARCH, and STN monitoring sites within the 12 km modeling domain. VISTAS states are outlined in bold.

3. Model performance evaluations

Fig. 2 compares the CMAQ and CAMx model performance for OC and the 2002 36/12 km base case simulation using monthly fractional bias and fractional gross error statistical performance measures across the IMPROVE monitoring network in the 12 km grid (see Fig. 1). Monthly fractional bias (FB) and fractional error (FE) statistics are calculated using paired predictions (P_{ij}) and observations (O_{ij}) at site j across time periods i as follows:

$$\mathrm{FB} = \frac{1}{\mathrm{N} * \mathrm{M}} \sum_{i=1}^{\mathrm{N}} \sum_{j=1}^{\mathrm{M}} \left(2 \frac{P_{ij} - \mathrm{O}_{ij}}{P_{ij} + \mathrm{O}_{ij}} \right),$$

$$\mathrm{FE} = \frac{1}{\mathrm{N} * \mathrm{M}} \sum_{i=1}^{\mathrm{N}} \sum_{j=1}^{\mathrm{M}} \left| 2 \frac{P_{ij} - \mathrm{O}_{ij}}{P_{ij} + \mathrm{O}_{ij}} \right|,$$

where, N is the total number of monitoring sites and M is the total number of measurements during the averaging period.

The CMAQ and CAMx models used exactly the same horizontal and vertical grid structure, SMOKE emission model outputs, initial and boundary conditions, and meteorological inputs based on the same MM5 meteorological model simulation (Olerud and Sims, 2004). The MM5 outputs were processed by MCIP and MM5CAMx to generate the model-ready meteorological inputs for CMAQ and CAMx, respectively. Thus, differences in model performance are primarily due to model formulation. Although the seasonal tendency in the OC model performance is similar between the two models, the CMAQ underestimation tendency is greater, at around −80% in the summer, compared to approximately −60% for CAMx. OC model performance is affected by the accuracy of emissions inventories for primary OC particles and organic gases, both from anthropogenic and biogenic sources, and by the models' treatment of primary OC emissions, the formation of secondary organic aerosols (SOA), advection and diffusion, and the dry and wet deposition rates. Based on the comparison of predicted and observed OC concentrations alone, it is difficult to interpret which of these processes are contributing the most to the CMAQ and CAMx performance problems and differences in the two models' performance. Additional sensitivity tests identified the SOA modules in the two models as a major reason for the differences in the CMAQ and CAMx OC model performance.

The SEARCH network includes hourly measurements of total carbon mass (TCM) at all 8 sites, where TCM is defined as OC plus elemental carbon (EC). Fig. 3 displays time series of predicted and observed TCM for the CMAQ and CAMx models at the Atlanta, Georgia SEARCH site (Jefferson Street) for the 1–7 July 2002 period. The model predictions are expressed as stacked time series of each component of TCM in the model: EC, primary organic matter (POM), SOA due to anthropogenic VOC emissions (SOAA) and SOA due to biogenic VOC emissions (SOAB). The stacked time series plots display the concentration for each component of predicted TCM as the difference between two adjacent stacked time series. Measurements are not available to apportion the OC components of observed TCM. The CAMx model exhibits better TCM model performance in Atlanta than CMAQ with a lower fractional bias, −18% versus −57%, and lower fractional gross error, 35% versus 69%. The most striking feature of the CMAQ predicted TCM time series is the large diurnal variation in the TCM estimates with peaks in the early morning and minimums in the early evening. This large diurnal variation in the CMAQ predicted hourly TCM estimates is not fully reflected in the observations and is driven by SOA from biogenic terpene emissions (SOAB). Biogenic SOA is known to be

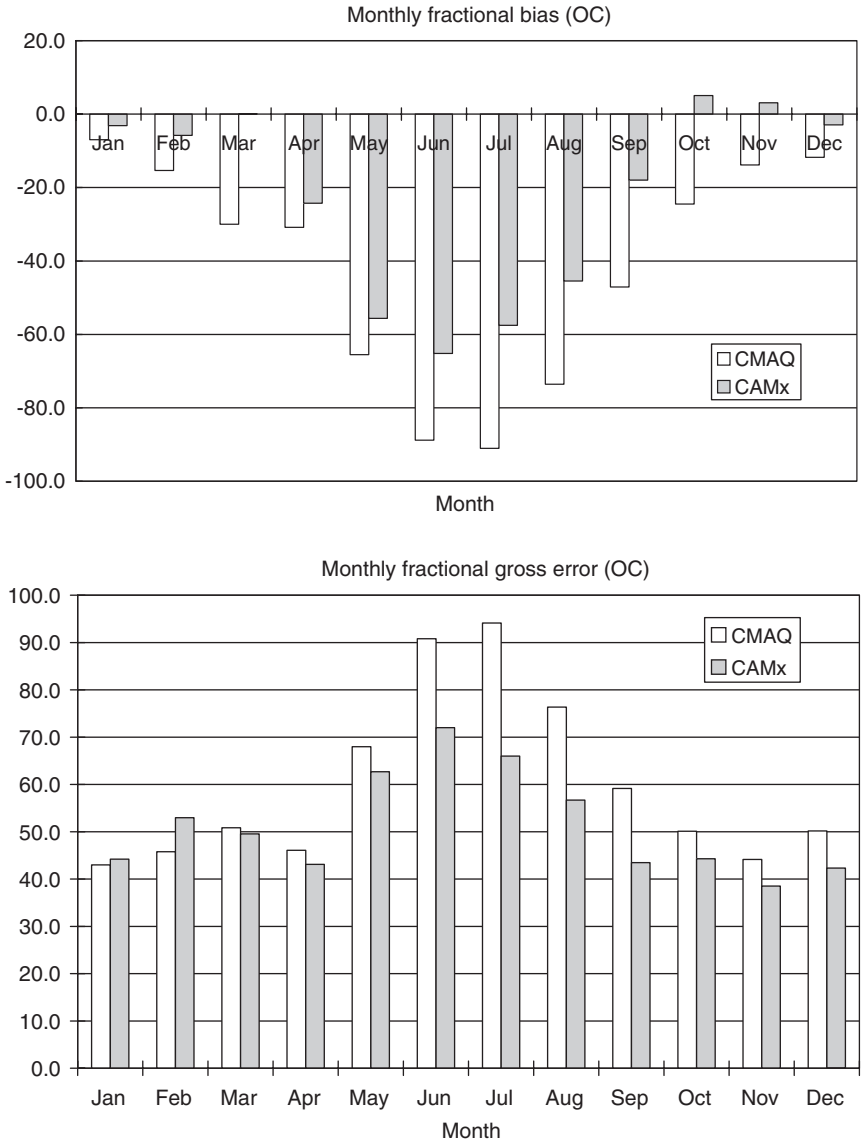

Fig. 2. Fractional bias and fractional gross error by month for organic carbon (OC) and the CMAQ V4.3 and CAMx models at IMPROVE monitors in the VISTAS 12 km modeling domain.

a major component of OC in the southeastern US, which is supported by recent carbon dating of OC measurements at SEARCH sites that indicate a majority (average ~60% at urban Atlanta and ~85% at rural Yorkville GA and Oak Grove MS sites) of the OC is due to modern carbon (e.g., biogenic SOA, biomass burning, etc.) not fossil carbon (e.g., gasoline, diesel and coal combustion) and such high biogenic OC concentrations occur in the summer even when fire contributions are not seen (Edgerton et al., 2003) indicating the major contributions due to biogenic SOA. Given the importance of biogenic SOA in the CMAQ OC model performance and its role in the differences in the two models' performance as shown in Fig. 3, we examined the biogenic SOA formulation in the two models.

3.1. CMAQ and CAMx biogenic SOA modules

Details on the formulation of the CMAQ and CAMx biogenic SOA modules are described in

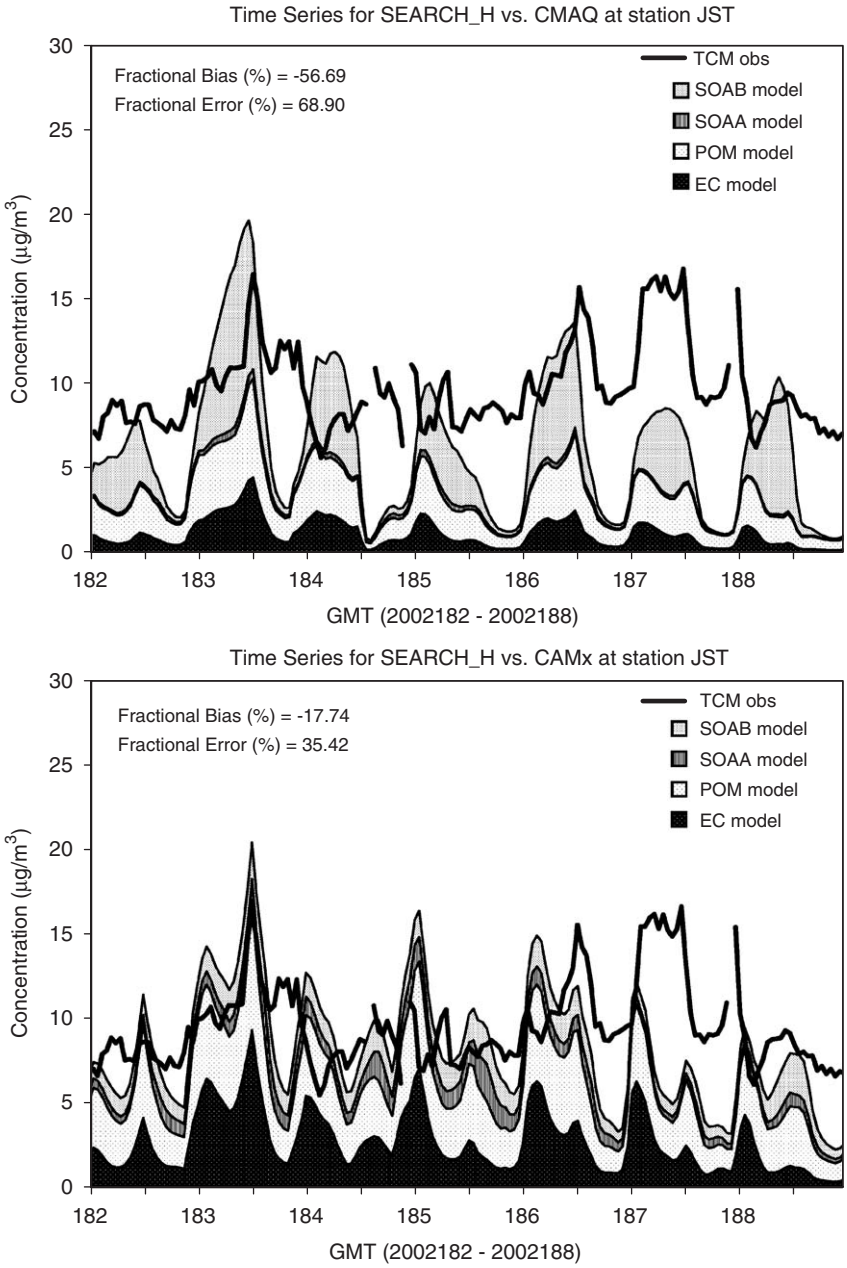

Fig. 3. Stacked hourly time series plots of observed (red), CMAQ V4.3 (top) and CAMx (bottom) estimated hourly TCM performance at the Atlanta, Georgia SEARCH site broken down by predictions of elemental carbon (EC), primary organic matter (POM), secondary organic aerosol due to anthropogenic VOC (SOAA) and secondary organic aerosol due to biogenic emissions (SOAB).

Binkowski and Roselle (2003) and Strader et al. (1999), respectively. Conceptually the two SOA modules are similar, but use several different assumptions and parameters. The biogenic SOA precursors were modeled with the biogenic emissions information system—Version 3 (BEIS3) model (Pierce et al., 2002). BEIS3 generates three biogenic VOC species: isoprene (ISOP), monoterpenes (TERP) and other biogenic VOC (OVOC). For this study, the Carbon Bond 4 (CB4) photochemical mechanism was used (Gery et al., 1989) that represents VOC compounds based on their carbon bond structure. The BEIS3 ISOP, TERP and OVOC species are speciated into the CB4

species for photochemical modeling in CMAQ and CAMx as follows (molar speciation):

- ISOP = ISOP (isoprene is an explicit species),
- ALD2 = 1.5 × TERP,
- OLE = 0.5 × TERP,
- PAR = 6.0 × TERP,
- NR = 0.5 × OVOC,
- OLE = 0.5 × OVOC,
- PAR = 8.5 × OVOC,
- TERPB = TERP.

Here, ALD2, OLE, PAR and NR are the CB4 chemical mechanism representations of the biogenic VOC emissions as high molecular weight aldehydes, olefinic carbon bond, paraffin carbon bond and non-reactive functional groups. In CMAQ, the TERPB species is specified in the emissions inputs, along with its CB4 representation of ALD2, OLE and PAR, but does not participate in the photochemical mechanism and is only used in the SOAB formation module. Whereas in CAMx, TERP is speciated into the CB4 species as listed above, only the speciated olefin component is represented by a separate OLE2 species. The biogenic OLE2 species participates in the photochemical mechanism with identical reactivity properties of the anthropogenic OLE CB4 species, only when OLE2 is oxidized, it generates a condensable gas (CG) that can form SOA. In CMAQ, the TERPB species forms a SGTOT (CG + SOA) species based on oxidation parameters extracted from the photochemical module. SGTOT consists of the combined gaseous CG plus particle SOA that are assumed to be in equilibrium. CMAQ transports the SGTOT species and splits it to CG and particle SOA for output, whereas CAMx separately transports the CG and SOA species.

There are three main parameters that define SOA formation in the CMAQ and CAMx modules:

- Y = Yields: The amount CG/SGTOT species that is formed from the oxidized VOC;
- Cstar = Condensation concentration: The concentrations at which the CG begins to condense into a particle SOA; and
- Hvap = Heat of vaporization: Thermodynamic parameter that accounts for more SOA under colder temperatures.

Table 1 lists the biogenic SOA parameters used in the CMAQ (V4.4) and CAMx models. The CAMx SOA parameters are based on Strader et al. (1999), whereas the CMAQ SOA parameters are based on a fit to more recent smog chamber data collected at the California Institute of Technology for several biogenic monoterpene species (Binkowski and Roselle, 2003). The Strader et al. (1999) biogenic SOA parameters used in CAMx were implemented in CMAQ. The model was tested the model for the July 2002 period and produced improved OC and TCM model performance (ENVIRON et al., 2004). For example, the average fractional bias for TCM across the seven SEARCH sites (see Fig. 1) was reduced from –57% to –21% using the Strader/CAMx SOA parameters over using the SOA parameters in CMAQ. The main reasons for the improved OC model performance using the Strader et al. (1999) SOA parameters is due to the Cstar that is two orders of magnitude lower than used in CMAQ. However, the Strader et al. (1999) biogenic SOA parameters are based on older data than the CMAQ values and do not match the more recent smog chamber measurements as well (ENVIRON et al., 2004). This suggests the better model performance of CMAQ with the Strader et al. parameters may be fortuitous. Therefore, the original CMAQ SOA parameters for monoterpenes were retained and used in the additional sensitivity analyses presented here. Furthermore, a persistent OC underestimation bias remains and other possible reasons for the poor OC model performance were investigated.

Table 1
CMAQ 2-product SOA parameters (Binkowski and Roselle, 2003) and Strader et al. (1999) 1-product SOA parameters used in CAMx

	CMAQ (2-product)	CAMx (1-product)
Yields (ppm/ppm)	0.066 0.296	0.068[a]
Cstar ($\mu g/m^3$ at 298 K)	0.865 11.804	0.008
Hvap (KJ/mol)	156	0

[a]Converted for the CMAQ TERPB species.

3.2. Investigations of organic carbon formulation

A review of recent literature of biogenic SOA measurements identified several processes that may

be important to biogenic SOA formation that are not treated by the BEIS3 biogenic emissions and the CMAQ and CAMx SOA modules:

Polymerization: Recent measurements indicate that some SOA species may polymerize, resulting in species that are no longer volatile and cannot evaporate back to a CG. In this case, the equilibrium assumption between the CG and SOA will understate the amount of particle SOA present in the atmosphere (Kalberer et al., 2004; Jang et al., 2002).

Sesquiterpenes: Sesquiterpenes are not accounted for in the BEIS3/CMAQ/CAMx SOA modeling system (Guenther et al., 2000; Vizuete et al., 2004).

Isoprene: More recent evidence suggests that isoprene can also form particle SOA compounds that are not accounted for in CMAQ or CAMx (Claeys et al., 2004; Matsunaga et al., 2003, 2005; Holzinger et al., 2005).

Biogenic OVOC: SOA may also form from the OVOC species that should be accounted for (Matsunaga et al., 2003, 2005).

Reactivity: In both CMAQ and CAMx, when an SOA precursor is oxidized to form a CG the reactivity of the CG is not accounted for.

Acid catalyzation: Recent literature also suggests that some SOA formation may have acid catalyzed reactions (Claeys et al., 2004; Jang et al., 2005).

Heterogeneous reactions: Recent evidence suggests that some SOA formation may occur during heterogeneous aqueous-phase chemical reactions (Yu et al., 2005).

A prototype module was added to CMAQ that accounted for the first three processes listed above. The last four processes were not included in this work because there are not enough quantitative experimental data yet to establish a parameterization. Modules were added to the CMAQ SOA module under the following constraints:

- The existing CMAQ SOA module for monoterpenes would remain unchanged;
- The same CMAQ model inputs would be used; and
- The basic CMAQ model formulation would remain unchanged, modules would be added to account for polymerization and SOA from sesquiterpenes and isoprene.

The OC model performance and CMAQ/CAMx comparison discussion given above and in Figs. 2 and 3 used CMAQ Version 4.3 (V4.3). However, during the course of the analysis a newer version of CMAQ was released (Version 4.4) that was used when implementing the SOA module enhancements. It should be noted that CMAQ V4.4 exhibited

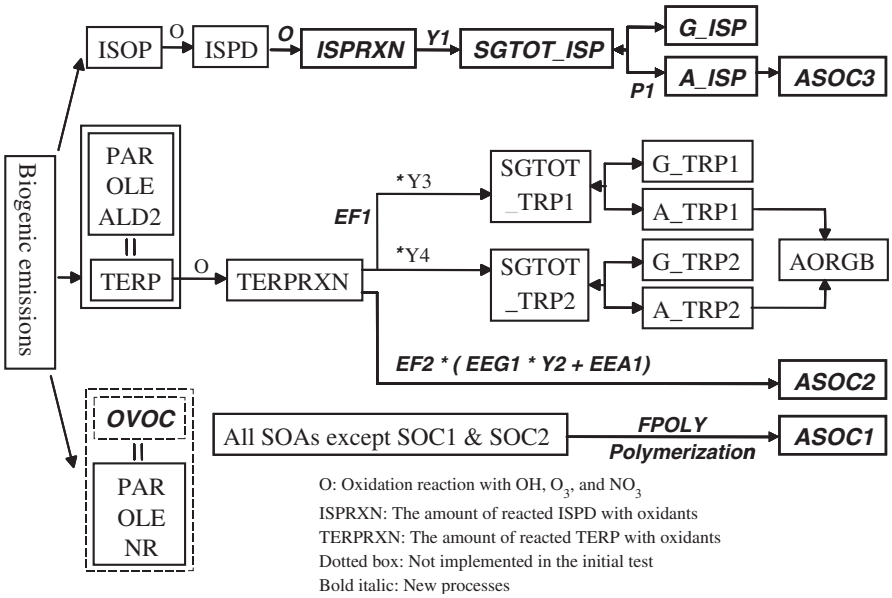

Fig. 4. Schematic describing the addition of new SOA processes (bold italic) within the existing CMAQ SOA module (regular font) to treat polymerization and SOA from sesquiterpenes and isoprene.

similar OC model performance attributes as CMAQ V4.3, only with V4.4 exhibiting even worse (~−100%) summer underestimation bias than V4.3 (~−80%).

4. Enhancement of the CMAQ SOA module

Fig. 4 displays how the prototype representation of new processes to represent SOA polymerization and SOA formation from sesquiterpenes and isoprene were added to the CMAQ SOA module using the existing CMAQ structure and inputs. The new components of the SOA module are indicated in bold italic, whereas the existing CMAQ SOA components (Binkowski and Roselle, 2003) use a regular font. There are several parameters that must be defined in the new elements of the enhanced SOA module: emission factors (EF), canopy escape efficiencies for gases (EEG) and aerosols (EEA) and SOA yields (Y). Based on an analysis of recent measurements, primarily from a recent biogenic emissions field study in Duke Forest, North Carolina (Stroud et al., 2005; Matsunaga et al., 2005), a range of values for the factors in Fig. 4 were developed as shown in Table 2. For the initial prototype of the enhanced SOA module, we selected the mid-point of the range values for the factors from the measurements (Table 2). No attempt was made to optimize the parameters in Table 2 for OC/TCM model performance.

The emission factors, EF1 and EF2, relate the monoterpene emissions estimated by BEIS3 to emissions of monoterpenes, EF1 (e.g., α-pinene), and sesquiterpenes (EF2). Table 2 displays the range of EF1 and EF2 factors based on recent field study data (Stroud et al., 2005). Using the midpoint of the range results in emission factors of 0.7 for EF1 and 0.4 for EF2. EF1 is assigned a value of 0.7 based on field observations that indicate that the BEIS3 terpene emission factors are likely overestimated due to a tendency of earlier measurements approaches to artificially increase the emissions due to disturbance when leaves were enclosed in the measurement system. As an initial approach for including sesquiterpene emissions, we have assigned EF2 a value of 0.4 based on the ratio of the observed sesquiterpene emission from the Duke Forest field study (Stroud et al., 2005) to the BEIS3 monoterpene emission estimate. The net result is that BEIS3 TERP emissions are increased by 10% and split 64% as monoterpenes and 36% as sesquiterpenes. The CG yields from the sesquiterpenes are assumed to partly condense into a non-volatile SOA particle that is modeled in CMAQ using the new secondary organic carbon species (SOC2) species and only some of the gas and aerosol species associated with sesquiterpenes is assumed to escape from the canopy using the mid-range of the escape efficiencies (EE) estimated by Stroud et al. (2005). The fraction of BEIS3 TERP emissions that are assumed to be monoterpenes (i.e., 64% of the emissions) are treated with the standard CMAQ two-product SOA module (Table 1) assuming equilibrium between the CG and SOA with the SOA output in the standard AORGB species (Binkowski and Roselle, 2003). The isoprene SOA formation pathway forms a CG using the mid-point yield rate based on the range of recent measurements (Stroud et al., 2005) and a CG/SOA partitioning rate based on the mid-point of measurements from Matsunaga et al. (2003, 2005) (Table 2). The isoprene SOA is assumed to be volatile and is modeled as a new secondary organic carbon species in CMAQ (SOC3). Finally, all SOA species, with the exception of the already non-volatile SOC1 (polymerized SOA) and SOC2 (sesquiterpene) species, are assumed to partially polymerize into non-volatile particles that are stored in the SOC1 species. The polymerization rate is based on the results of Kalberer et al. (2004) who found that 50% of the SOA polymerized in 20 h.

Table 2
Parameters use in enhanced SOA module (see Fig. 4)

Parameter	Mid-point	Range
EF1	0.7	0.4–1.0
EF2	0.4	0.2–0.6
EEG1	0.325	0.2–0.45
EEA1	0.2	0.05–0.35
Y2	0.875	0.75–1.0
Y1	0.11	0.06–0.16
P1	0.45	0.15–0.75

EF1 is the emission factor of monoterpenes to the TERP emissions estimated by BEIS3; EF2 the emission factor of sesquiterpenes relative to the TERP emissions estimated by BEIS3; EEG1 the escape efficiency of gas phase precursor of sesquiterpenes from canopy; EEA1 the escape efficiency of SOA from sesquiterpenes from canopy; Y1 the SOA yield of oxidated isoprenes; Y2 the SOA yield of sesquiterpenes; P1 the partitioning ratio of SOA from isoprene.

4.1. CMAQ simulation with the enhanced SOA module

The standard CMAQ Version 4.4 (V4.4) and CMAQ with the enhanced SOA module were

exercised for the January and July 2002 period using a modeling domain covering the continental US with a 36 km grid. The model was initialized using 13–15 spin up days. The two versions of the model were evaluated using OC and TCM measurements from the IMPROVE, STN, and SEARCH networks in the southeastern US (see Fig. 1). Fig. 5 displays the stacked time series of each component of TCM at Jefferson Street in Atlanta, GA, as predicted by CMAQ with the modified SOA module. In this plot, SOC1 (polymerized SOA) is included in POM since this species is regarded as non-volatile and SOC2 (sesquiterpene) and SOC3 (ISOP) are included in SOAB. At the Jefferson Street site for the 1–7 July 2002 period, the fractional bias was improved from a –57% underestimation to near zero (1.5%) and fractional errors improved from 69% to 41%. POM and biogenic SOA are notably larger using the enhanced SOA module (Fig. 5) than in the original SOA module (Fig. 3), while anthropogenic SOA is unchanged. The diurnal periodicity of POM is reduced using the enhanced SOA module, suggesting that polymerization of SOA reduces the nighttime volatilization of SOA as predicted by the original SOA module. Fig. 6 displays the monthly average fraction of each TCM component at Jefferson Street predicted by the modified CMAQ for July 2002. The most dominant component of TCM is SOA from sesquiterpenes (SOC2), which comprises 33% of the estimated TCM, with SOA from monoterpenes (SOAB), polymerized SOA (SOC1) and primary emitted organic matter (POM) being the next most important components

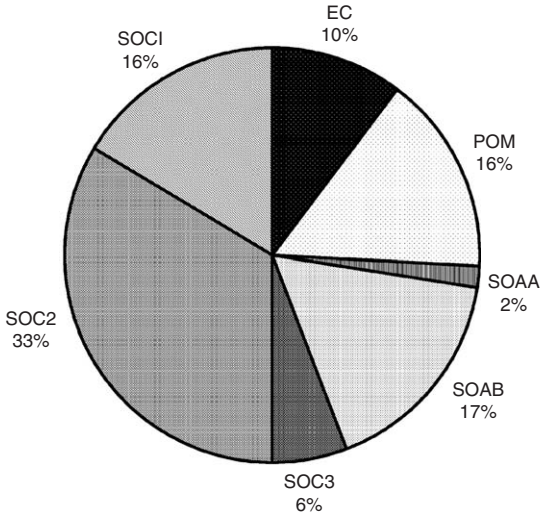

Fig. 6. Monthly (July) average composition of carbonaceous components predicted by CMAQ with SOA updates at the Atlanta, George SEARCH site.

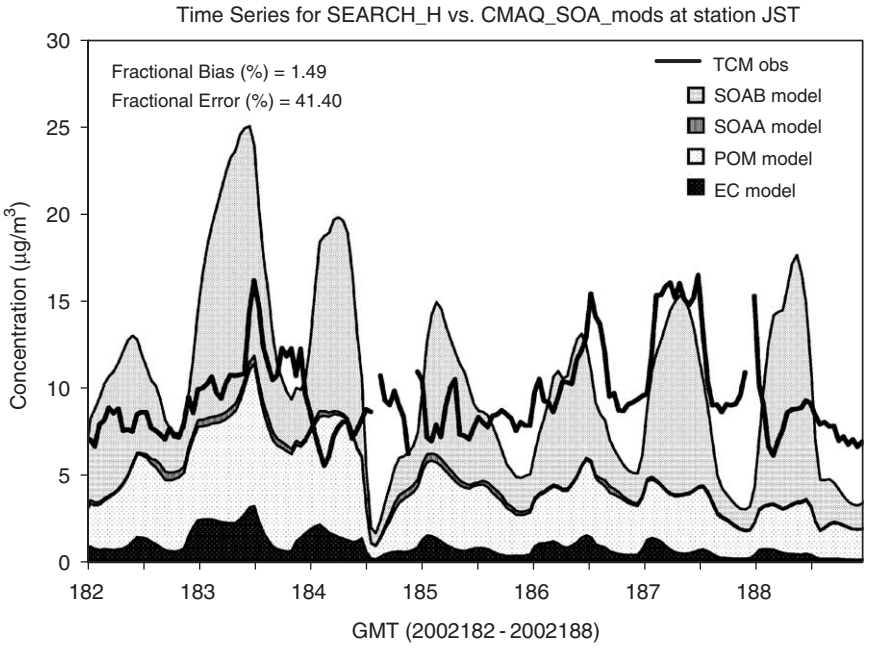

Fig. 5. Stacked hourly time series plots of TCM performance by CMAQ V4.4 with SOA updates at the Atlanta, Georgia SEARCH site; Shown the same way as in Fig. 3 except that POM here includes SOC1 and SOAB includes SOC2 and SOC3.

(16–17%) of the monthly average TCM at the Jefferson Street, Atlanta site. Results are similar for other urban and rural SEARCH sites with the urban sites exhibiting higher contributions due to primary emitted organic matter (POM) than the rural sites. Fig. 7 displays the 24-h OC model performance across the IMPROVE (top) and SEARCH (bottom) networks in the southeastern US for July 2002 and the standard CMAQ V4.4 (diamonds) versus the SOA enhanced version of CMAQ (crosses). The SOA enhancements in CMAQ results in substantially improved OC model performance across the IMPROVE and SEARCH networks in the southeastern US. The OC underestimation bias, represented by fractional bias values of −103% and −118% across the IMPROVE and SEARCH networks, respectively using the standard CMAQ V4.4, is reduced substantially to fractional bias levels of −2% and −27%, respectively, using CMAQ with the SOA enhancements. The OC fractional errors are also reduced, from 105% and 118% using the standard CMAQ V4.4 to 39% and 48% when CMAQ with the SOA enhancements is used.

These improvements in model performance are not just limited to the southeastern US. Table 3 displays the OC fractional bias for the southeastern, northeastern, midwestern, central and western US regions using the standard CMAQ V4.4 and CMAQ with the enhanced SOA module and OC measurements from the IMPROVE and STN networks. The OC fractional bias is reduced from a large underestimation tendency (−67% to −105%) using CMAQ V4.4 to biases closer to zero (−14% to +12% for IMPROVE and −44% to −24% for STN) using CMAQ with the enhanced SOA module in four of the five US subregions. Only in the western US do we see some degradation in model performance due to the SOA enhancements in July 2002; biogenic emission rates derived for vegetation in the southeastern US may overestimate emissions in the more arid western states. It should also be noted that the improvement is more noticeable at rural sites (IMPROVE) than at urban sites (STN). This is because the modified SOA module primary effect is to increase SOAB that has a greater influence at rural than urban sites. It should also be noted that the STN OC measurements are not blank corrected which is believed to result in an approximate 30% positive bias in the STN OC measurements. Accounting for this measurement artifact reduces the OC fractional bias using CMAQ

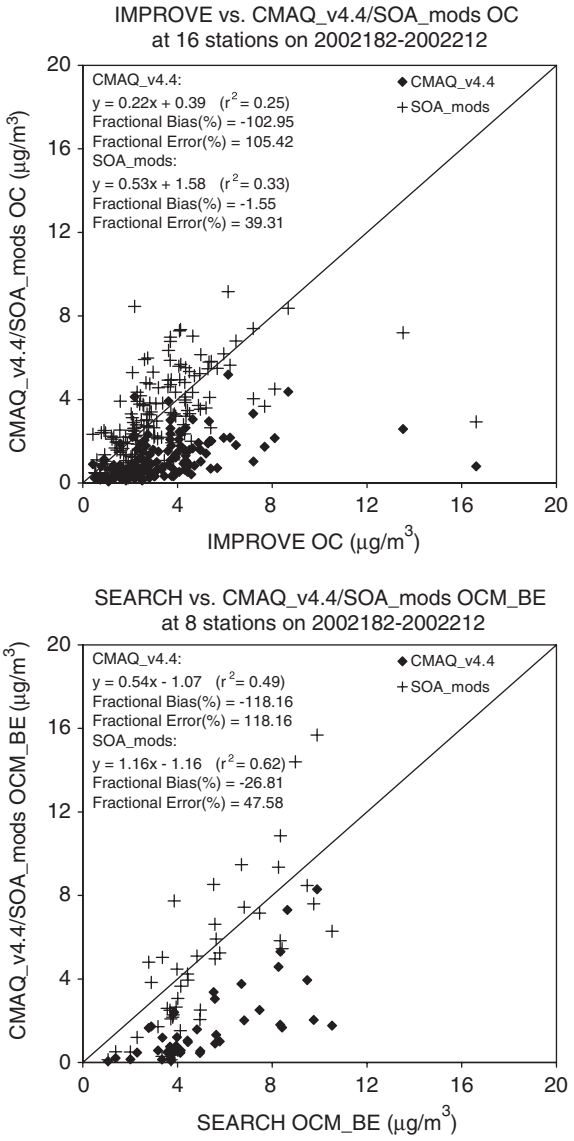

Fig. 7. Comparision of organic carbon (OC) model performance across the IMPROVE (top) and SEARCH (bottom) monitoring networks in the southeastern US for the standard CMAQ Version 4.4 (V4.4 base D; diamonds) and CMAQ with the enhanced SOA module (SOAmods; crosses).

with the enhanced SOA in the four eastern US subregions to near zero. The SOA updates have very little effect on OC and TCM model performance in January 2002. For example, across the IMPROVE sites in the southeast US the OC fractional bias in January 2002 changes from −2% for CMAQ V4.4 to +5% for CMAQ with the SOA enhancements. This is because both biogenic emissions and photochemical activity are much lower in the colder

Table 3
Summary of organic carbon (OC) model performance for the average fractional bias for the standard CMAQ V4.4 and CMAQ with the SOA enhancements (SOAmod), for July 2002 and different geographic regions of the US using the IMPROVE and STN networks

Fractional bias	IMPROVE OC		STN OC	
	V4.4 (%)	SOAmod (%)	V4.4 (%)	SOAmod (%)
Southeastern US	−102	−2	−105	−32
Midwestern US	−76	+12	−67	−24
Northeast US	−82	−14	−95	−44
Central US	−98	+8	−81	−27
Western US	+40	+84	−13	+18

winter months resulting in little SOA formation. Since, the CMAQ V4.4 OC performance in the winter months was already fairly good (see Fig. 2), these minor changes in OC estimates due to the SOA enhancements do not degrade the CMAQ winter OC model performance.

5. Summary and recommendations

The model performance evaluation of the CMAQ and CAMx models for the 2002 annual period and the continental US showed that chemical processes neglected in both models might be important missing factors in estimating OC concentrations. This paper demonstrates improved model performance when SOA formation from three mechanisms not currently addressed in either model are added to the CMAQ SOA module. In particular, we have identified the following processes that may be important for SOA formation that are not currently treated, or at least fully treated, in either the CMAQ or CAMx models:

- Polymerization of SOA into a non-volatile particle;
- SOA formation from sesquiterpenes;
- SOA formation from isoprene;
- SOA formation from OVOC;
- Effects of acid catalyzed reactions on SOA formation;
- Heterogeneous SOA formation through aqueous-phase chemistry; and
- Effects of photochemistry on CG concentrations.

Using recent information in the literature and field study data from the Duke Forest, North Carolina, a prototype representation of the effects of the first three processes listed above was developed and implemented in the CMAQ SOA module (i.e. polymerization of SOA, and SOA formation from sesquiterpenes and isoprene). The prototype representation of these processes should be considered a first cut approximation and a placeholder for accounting for these processes in the model. Additional experiments and studies are needed to refine these representations. Furthermore, these approximations are based primarily on biogenic emission field studies carried out at the Duke Forest, North Carolina. Thus, the parameters selected may not be representative of other portions of the US, particularly in the western states that has distinct biomass types compared to the eastern US. This may explain in part why substantial improvements in OC performance is seen with the SOA enhancements throughout the US except the western US.

While model performance was improved using the enhanced SOA module in CMAQ, we recognize that other factors not evaluated in this paper also contribute to overall model performance. For example, improvements to emissions inventories for primary OC particles and organic gases would also affect model performance and might affect the conclusions in this paper.

Further research on the formation of SOA from anthropogenic and biogenic VOC emissions is needed. Additional evaluation of the CMAQ OC performance using the standard (Version 4.4) and enhanced SOA modules will be made using OC measurements that have been analyzed using receptor modeling to estimate the fraction of OC that is primary emitted versus SOA at the SEARCH sites and OC measurements that have been analyzed using C^{14} analysis to estimate the fraction of OC that comes from new versus fossil carbon emissions (Edgerton et al., 2003). Sources of OC from new carbon include biomass burning (e.g., wildfires, prescribed burns, agricultural burns and wood stoves and fireplaces) and SOA from biogenic sources, whereas sources of OC from fossil carbon include OC from combustion sources and SOA from combustion produced VOC emissions. The evaluation of the CMAQ OC estimates using the primary versus secondary OC splits and new versus fossil carbon splits will allow an assessment of the prototype SOA biogenics module. Given the uncertainties associated with particle carbon measurements, further evaluation against elemental carbon

in addition to OC is also warranted. In the longer term, additional laboratory, smog chamber and field experiments are needed along with improved representation of emissions and SOA formation mechanisms to develop a more definitive SOA module for air quality modeling. In addition, better representation of biogenic SOA precursor emissions is needed to drive the next generation of SOA modules.

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