UPDATES TO THE TREATMENT OF SECONDARY ORGANIC AEROSOL IN CMAQv4.7

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1. INTRODUCTION

Widely used in both regulatory and academic applications, the CMAQ model has frequently produced negatively-biased surface predictions of fine particulate matter (PM2.5), when compared to observations collected during summer months at networks such as STN, IMPROVE, and SEARCH. This bias is often dominated by low predictions of the organic carbon fraction. Furthermore, diurnal and seasonal patterns of carbonaceous aerosol measurements differ from those simulated by the model (Morris et al., 2006). Secondary organic aerosol (SOA) composes a large fraction of total carbon during the summer and has been the focus of a large body of research aimed to better understand the chemistry and physics of its formation and transport. SOA is formed from semi-volatile products of hydrocarbon oxidation. It is then absorbed onto preexisting organic mass in the atmosphere where it experiences further transformations.

In an effort to improve model performance with respect to surface measurements and to improve the underlying scientific processes and assumptions, the SOA module in CMAQ has been updated to include several recently identified formation pathways and precursors. The module was made compatible with both SAPRC99 and CB05 chemical mechanisms through modification of each.

2. SECONDARY ORGANIC AEROSOL MODULE DESCRIPTION

The underlying SOA module in CMAQ is based on the absorptive partitioning theory as adapted by Schell et al. (2001). Potential SOA precursors are oxidized by free radicals including OH, O_3, and NO_3. Some of the products of these reactions are condensable and contribute to SOA productions. The amount of condensable product produced in the reaction relative to the amounts of reacting precursor, or the stoichiometric yield, is obtained from smog-chamber studies. The condensable material is then partitioned between gas and particle phases based on the saturation concentration, $C^*_{sat,i}$, and its mole fraction in the mixture of different organics according to Raoult's Law:

$$C_{aer,i} = C_{tot,i} - \frac{\dfrac{C_{aer,i}C^*_{sat,i}}{MW_i}}{\displaystyle\sum_{j=1}^{n}\dfrac{C_{aer,j}}{MW_j} + \dfrac{C_{POC}}{MW_{POC}}},$$

where, in a mixture of n SOA species, $C_{aer,i}$ is the aerosol concentration of species i, $C_{tot,i}$ is the total condensable mass in both phases, C_{POC} is the concentration of existing primary organic carbon, and MW is the molecular weight.

The CMAQ SOA module was expanded to include seven SOA precursors and 18 particle phase species compared to the previous five precursors and four species (Table 1). The species list has been extended to track each formation pathway in order to more easily determine the absolute contributions from each SOA precursor. At the same time, the Aitken mode SOA species were removed to reduce the number of advected species. There is currently a lack of definitive measurements of these types of particles and this removal proved to cause a negligible impact on model predictions of SOA mass.

A detailed description of each pathway follows.

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Table 1. Modeled Secondary Aerosol Species.

CMAQv4.6 and prior (aero4)		CMAQv4.7 (aero5)	
Precursor	SOA	Precursor	SOA
Alkane		Alkane	AALKJ
Xylene	AORGAI	Xylene	AXYL1J, AXYL2J, AXYL3J
Toluene	AORGAJ	Toluene	ATOL1J, ATOL2J, ATOL3J
Cresol		Benzene	ABNZ1J, ABNZ2J, ABNZ3J
Monoterpene	AORGBI	Monoterpene	ATRP1J, ATRP2J
	AORGBJ	Isoprene	AISO1J, AISO2J, AISO3J
		Sesquiterpene	ASQTJ
		Glyoxal/Methylglyoxal	AORGCJ
		SV Anthro. SOA	AOLGAJ
		SV Biog. SOA	AOLGBJ

"I" following the aerosol species name denotes Aitken mode, while "J" denotes accumulation mode.

2.1 Aromatic Precursors

In addition to the previously considered xylene and toluene, benzene was added as a precursor to aromatic SOA. Cresol was removed to avoid double counting as it is already an aromatic oxidation product. It was also found that cresol contributed only a minor fraction of SOA.

Parameterization for the three aromatic precursors was adapted from Ng et al. (2007a). Each precursor is allowed to react with OH to produce aromatic peroxy radicals that continue to react with either NO or HO_2, depending on NO_x availability. Chamber-based aromatic yields were adjusted to account for the presence of the intermediate species (peroxy radical) in the chemical mechanism.

The addition of benzene as an SOA precursor required some alteration to the emissions processor in order to transport it as an explicit species in the SAPRC99 mechanism.

2.2 Alkane Precursors

Alkane SOA parameterization was unchanged, but significant development and evaluation efforts are planned to improve this component in the next CMAQ release.

2.3 Isoprene Precursors

Isoprene was added as a new precursor of SOA following the two-product model parameterization from Henze and Seinfeld (2006). Additionally, the enhancement of SOA production under acidic conditions was added based on a chamber study by Surratt et al. (2007). The additional isoprene created through acid enhancement effects was considered non-volatile. Particle phase acidity was estimated through a charge balance and was limited by the range of experimental conditions (H^+ between 0.0 and 530.0 nmol/m^3). In order to assure mass balance, the acid catalyzed fraction was also constrained by the total available semi-volatile isoprene.

2.4 Sesquiterpene Precursors

Sesquiterpenes were added as the third new SOA precursor in the module, using available measurements for β-caryophyllene and α-humulene. Partitioning to the particle phase was considered for a single semivolatile product following Griffin et al. (1999) with adjustments to the stoichiometric yield based on recent density measurements (Bahreini et al., 2005; Ng et al. 2007b).

2.5 Monoterpene Precursors

SOA partitioning parameters for monoterpenes were unchanged in the module. However, particle mass contributions from this precursor differ significantly due to the changes of enthalpies of vaporization of all SOA species as detailed in Section 2.8..

2.6 Cloud Processes

Glyoxal and methyglyoxal were added as SOA precursors through heterogeneous reactions in cloud water based on Carlton et al. (2007) and Altieri et al. (2008). These precursors partition into the aqueous phase according to Henry's Law and react with $OH_{(aq)}$. The products of these reactions remain in the particle phase as the cloud droplets evaporate. The resulting SOA species was considered nonvolatile, because these products have high molecular weights and exhibit other oligomeric qualities (Carlton et al., 2007; Altieri et al., 2008).

Since the CB05 mechanism does not have an explicit glyoxal species (only methylglyoxal), the relevant parameters, such as MGLY solubility, were modified in this mechanism to achieve parity with SAPRC99 predictions.

2.7 Oligomerization Processes

The semi-volatile SOA species were allowed to polymerize according to the findings of Kalberer et al. (2004), who estimated that after approximately 20 hours of aging, 50% of organic mass consists of polymers. Thus, a 20 hour 'half-life' was applied to the species from alkane precursors, aromatic precursors under high NO_x conditions, monoterpenes, sesquiterpenes, and acid-neutral isoprenes. Two species were introduced to track SOA oligomers – AORGAJ for those originating from anthropogenic emissions and AORGBJ for biogenic species from biogenic emissions.

2.8 Parameter Updates

As a major modification, the enthalpies of vaporization, ΔH_{vap}, of the semi-volatile components were changed to reflect recent laboratory experiments. Previously, a single value of 156 kJ/mol was used for all species. This value was fairly high compared to values of 15-88 kJ/mol found in the current literature. The selected ΔH_{vap} values (Table 2) were based largely on the laboratory data of Offenburg et al. (2006).

Table 2. Enthalpies of vaporization

Compound	ΔH_{vap} kJ/mol
SV ALK	40.0
SV XYL	32.0
SV TOL	18.0
SV BNZ	18.0
SV TRP	40.0
SV ISO	40.0
SV SQT	40.0

3. MODULE EVALUATION

To demonstrate the impact of the above outlined changes on the predictions of CMAQ SOA, two month-long simulations were conducted for January and August 2006 for both the original and expanded version of the SOA algorithms.

The results show an improvement in the seasonal patterns of SOA predictions. In particular, total biogenic SOA (monoterpenes, isoprene, sesquiterpenes, and their oligomers) decreased substantially in January, while greater concentrations were predicted in August (Figure 1).

Similarly, the high nighttime peaks simulated by the previous SOA module were decreased, as illustrated by the results for a modeled location in rural Georgia (Figure 2).

Furthermore, modeled SOA components were compared to carbon tracer measurements taken at a site in Research Triangle Park (RTP), NC in August and September of 2003. Tracers for isoprene, sesquiterpene, monoterpene, aromatics, biomass burning, "other" organic carbon and elemental carbon were available at the site (Kleindienst et al., 2007). The comparison shows an improvement over the previous model version, but modeled concentrations are still significantly lower than indicated by the measurements (Figure 3).
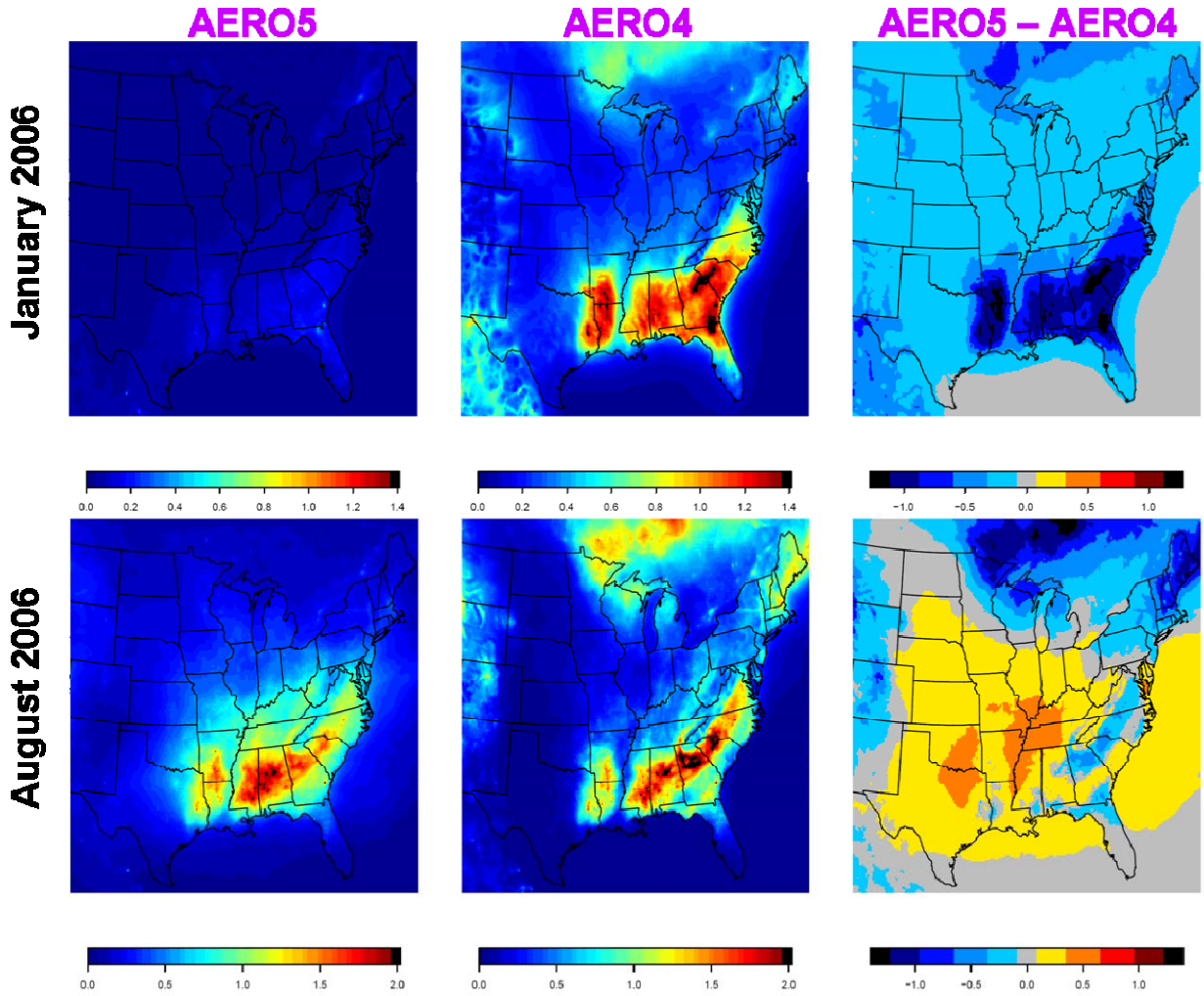
Figure 1. Average monthly biogenic SOA in ug/m^3 (originating from monoterpenes, isoprene, and sesquiterpene precursors)

4. DISCUSSION

Preliminary testing of the updated SOA module reveals several improvements including better diurnal and seasonal patterns of SOA predictions, higher concentrations of secondary organics from anthropogenic sources, and better spatial patterns of biogenic SOA. The scientific improvements described above were achieved with minimal increases to model CPU time (17% increase mainly as the result of more advected species). This code will be released to the public as part of the AERO5 module in CMAQ v4.7.
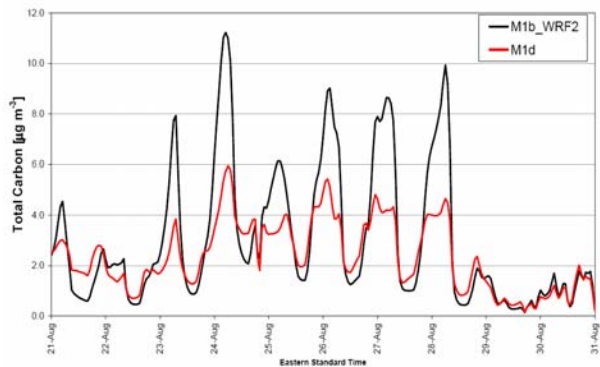

Figure 2. Modeled diurnal patterns of total carbon for the new SOA module (red) compared to the old module (black).
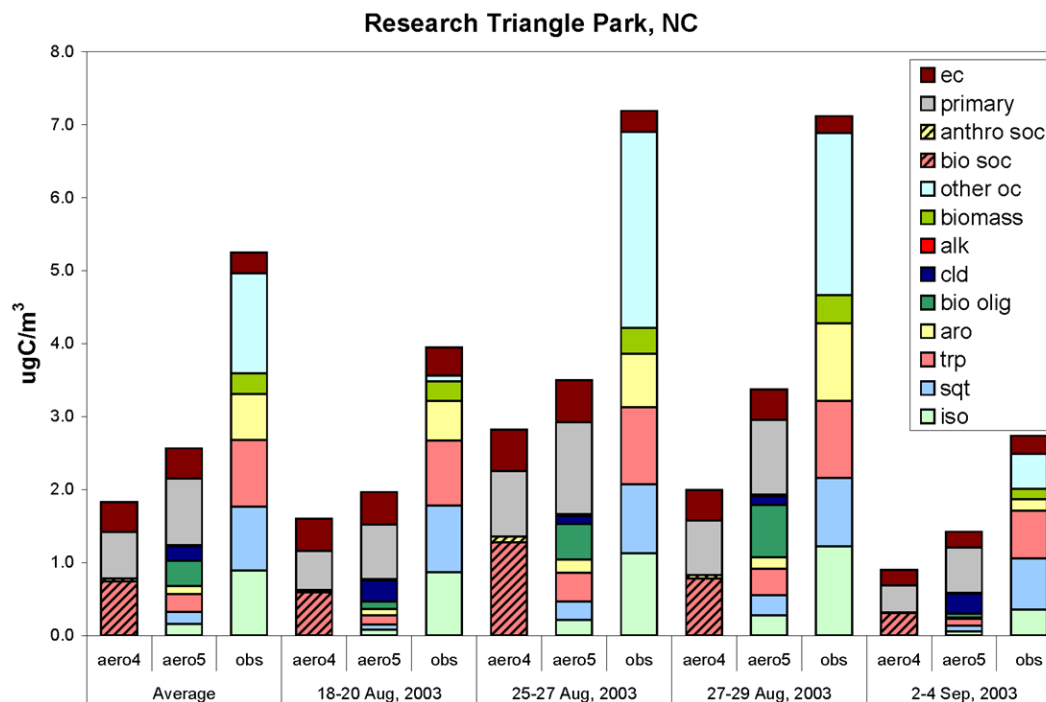
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Figure 3. Model comparison to tracer measurements taken at RTP, NC during four summer sampling periods, and their average.

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