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Incorporating Chemical Activity and Relative Humidity Effects in Regional Air
Quality Modeling of Organic Aerosol Formation

by

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A thesis submitted in partial fulfillment of the
requirements for the degree of

Master of Science
in
Civil and Environmental Engineering

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Abstract

Atmospheric particulate matter is known to have significant effects on human health, visibility, and global climate. The magnitudes of these effects, however, depend in complex ways on chemical composition, relative humidity, temperature, phase state, and other parameters. Current regional air quality models such as CMAQ (Community Multiscale Air Quality model) ignore many of these considerations, and consider that the formation of secondary organic aerosol (SOA) can be calculated by assuming thermodynamic ideality in the organic particulate matter (OPM) phase as well as negligible uptake of water into the OPM phase. Theoretical predictions and model simulations considering non-ideality and water uptake show that the standard model assumptions can lead to large errors in predicted SOA mass, and that the magnitude of these errors is sensitive to the composition of the OPM phase.

The SOA module in CMAQ v4.7.1 has been revised in this work to allow consideration of the effects of both non-ideality and water uptake. First, a reasonable specific surrogate structure was assigned to each of the lumped products assumed to be produced by reaction of the different precursor hydrocarbons considered in CMAQ (e.g., isoprene, benzene, and toluene). Second, the CMAQ code was modified to allow iterative calculation (at each point in space and time) of the gas/particle partitioning coefficient for each of the SOA-forming products and for water. Third, model simulations were performed for the Eastern US at a resolution of 36km x 36-km for late summer 2006, under a range of relative humidity conditions.

When compared with an appropriate base case, the modified code produced increases in SOA ranging from 0.17 to 0.51 $\mu\text{g}/\text{m}^3$. The average change was 0.30 $\mu\text{g}/\text{m}^3$, corresponding to a 37% increase in SOA formation. Incorporation of phase separation effects would likely lead to further increases in predicted SOA levels.

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1. Introduction and Background

1.1 Motivation

One cubic centimeter of ambient air typically contains between 10,000 and 100,000 tiny, suspended particles. These small liquid and/or solid particles are known as *particulate matter* (PM), with the gas + particle system then comprising an *aerosol*. Atmospheric PM can have significant effects on human health and air quality. The magnitudes of these effects, however, depend in complex ways on chemical composition, relative humidity, temperature, phase state, and other parameters. Current models ignore many of these considerations (Hallquist, et al., 2009). The aim of this work is to develop model-ready parameterizations of some of the complex interactions between atmospheric water vapor and organic PM and so address an aspect of atmospheric chemistry that is usually neglected in regional models.

1.2 Atmospheric PM: Overview

Atmospheric PM may contain organic compounds, inorganic salts, crustal substances, and water. The carbonaceous portion of PM is commonly divided into elemental carbon (EC) and organic carbon (OC) fractions. Nitrate and OC dominate PM mass in the western U.S., while sulfate and OC dominate in the South and East (NARSTO, 2004). In the Southeast, it is OC variations that are responsible for spatial distributions of overall PM levels (Lee, Wang, & Russell, 2010). In spite of its importance, the organic fraction is the least understood portion of PM (Seinfeld & Pankow, 2003).

Organic aerosols may be either emitted directly to the atmosphere (POA: primary organic aerosol) or formed via reactions of organic gases (SOA: secondary organic aerosol).

Currently, most field measurements and modeling studies have concluded that the majority of organic matter in the atmosphere is SOA (Goldstein & Galbally, 2007). SOA is important in terms of total aerosol mass, and because secondary formation tends to yield finer particulates than are present in primary aerosols. Overall, in the atmosphere, particles may range from several nm to nearly 100 μm in diameter. *Fine particulates* (generally defined as particles with diameters $< 2.5 \mu\text{m}$, and denoted $\text{PM}_{2.5}$) are of particular concern (Seinfeld & Pandis, 2006, pp. 58-60) due to their mechanisms of deposition in the respiratory tract and atmospheric behavior.

The smaller the particle, the farther it can travel into the human respiratory tract (Vallero, 2007, p. 380). Numerous studies have found correlations between PM concentrations and morbidity and mortality due to respiratory disorders, cardiovascular disease, birth defects, and cancer (Dockery & Pope, 1994; Peel, et al., 2005; Vrijheid, et al., 2011). In addition, there are indications that the composition of $\text{PM}_{2.5}$ may partially determine its health effects: studies have found associations between source-specific factors and both emergency department visits (Sarnat, et al., 2008) and mortality in the elderly (Mar, Norris, Koenig, & Larson, 2000).

The presence of fine particles is a leading cause of reductions in visibility (Eldering & Cass, 1996), with $0.1 - 1.0 \mu\text{m}$ particles having the largest extinction coefficients (Brasseur, Orlando, & Tyndall, 1999, p. 136). Finally, fine particles – due to their persistence, visibility effects, and ability to act as nuclei for cloud condensation – have a

large effect on global climate. The nature and magnitude of this effect, however, are uncertain, since aerosols can both absorb and scatter radiation (Seinfeld & Pandis, 2006, pp. 1054-1088). This leads to large uncertainties in climate models (IPCC, 2007). The poor understanding of OPM, in particular, has been identified as a major source of uncertainty in climate models (Kanakidou, et al., 2005).

1.3 Processes governing SOA Formation

SOA formation begins with the emission of volatile organic compounds (VOCs) into the atmosphere where they react with oxidizing agents such as ozone (O_3), hydroxyl radical (OH), and nitrate radical (NO_3). Oxidation makes the VOCs more polar and less volatile, and thus more prone to condense (Kroll & Seinfeld, 2008).

Figure 1. Overview of formation of secondary organic PM. Adapted from Seinfeld & Pankow, 2003.

1.3.1 Precursors

Biogenic VOCs (BVOCs). Globally, the majority of VOCs emitted to the atmosphere come from vegetation; bottom-up estimates put the global SOA mass formed from biogenic sources at 12-70 Tg C/year (Hallquist, et al., 2009). The most significant classes of BVOCs are the terpenoids, which include hemiterpenes (isoprene and 2-methyl-3-butene-2-ol), monoterpenes ($C_{10}H_{16}$), and sesquiterpenes ($C_{15}H_{24}$). Approximately half of all BVOCs consist of isoprene. Until recently, isoprene was not believed to lead to significant SOA formation (Kanakidou, et al., 2005), but it is now known that the potential of isoprene to form SOA is condition-dependent and potentially significant (Robinson, et al., 2011).

Anthropogenic VOCs (AVOCs). Many human activities -- primarily related to fossil fuel combustion and solvent usage -- emit VOCs. These fraction of these compounds that are aromatic hydrocarbons are particularly effective at forming SOA (see e.g. Henze, et al., 2008). Bottom-up estimates the anthropogenic fraction of global SOA mass put anthropogenic VOC emissions at 50-185 Tg C/yr, resulting in SOA formation of 3-17 Tg C/yr (Hallquist, et al., 2009). However, there is evidence that the AVOC mass might be much higher than had previously been expected (Volkamer, et al., 2006).

1.3.2 Oxidation

Generalized tropospheric VOC degradation reactions were described by Atkinson (2000), as shown in Figure 2. An oxidant initiates degradation of a VOC, yielding an alkyl radical ($R^\bullet$), which reacts with oxygen to form an alkyl peroxy radical ($RO_2^\bullet$). This in turn reacts with various oxidants present to yield low-volatility products.

Commonly investigated oxidants include OH, NO₃, and O₃. The initiating oxidant has a significant effect on the ultimate products formed, but this effect is not well-understood theoretically. There are also a limited number of laboratory experiments that have compared products formed as a function of initial oxidants (Kroll & Seinfeld 2008).

Figure 2. Depiction of VOC oxidation from Atkinson (2000). Intermediates include R• (alkyl radical), RO₂• (alkyl peroxy radical), and RO• (alkoxy radical).

One comparatively well-studied effect is that of ambient levels of nitrogen oxides (NO_x) (Henze, et al., 2008). Aromatic hydrocarbons show higher SOA yields under low-NO_x conditions; this is thought to be the result of aromatic peroxy radicals reacting with HO₂ and forming nonvolatile SOA (Ng, et al., 2007).

Another oxidant-related effect that has recently been the subject of investigation is that of acid-enhanced SOA formation, particularly from isoprene. Surratt (2007) found a close correlation between SOA formation and increased acidity at atmospherically relevant levels, consistent with acid-catalyzed particle-phase reactions.

1.3.3 Gas/Particle Partitioning

At equilibrium, a compound i will exist in both gas and particle phases. The compound's affinity for the particle phase can be parameterized with an equilibrium partitioning constant, $K_{p,i}$ (Mader & Pankow, 2002):

$$K_{p,i} = \frac{\text{concentration in particle phase}}{\text{concentration in gas phase}} \quad \text{Eqn 1}$$

Pankow (1994) uses the three components of a gas/particle partitioning system

- TSP ($\mu\text{g}/\text{m}^3$), the total suspended particulate material in the system
- A_i (ng/m^3), the gas-phase concentration of compound i
- F_i (ng/m^3), the particle-phase concentration of compound i

to define $K_{p,i}$ in $\text{m}^3/\mu\text{g}$ as

$$K_{p,i} = \frac{F_i/\text{TSP}}{A_i} \quad \text{Eqn 2}$$

Pankow (1994) then uses the activity-corrected Raoult's Law to relate the partial pressure of compound i at equilibrium with the organic particulate phase. Given Raoult's Law as:

$$p_i = X_{i,om} \zeta_i p_{L,i}^0 \quad \text{Eqn 3}$$

where $X_{i,om}$ is the mole fraction of i in organic material, ζ_i is the (mole-fraction scale) activity coefficient, and $p_{L,i}^0$ (atm) is the vapor pressure of i as a pure liquid at the system temperature. By using the Ideal Gas Law, Eqn. 2 may be written as:

$$K_{p,i} = \frac{R T f}{10^6 \overline{\text{MW}} \zeta_i p_{L,i}^0} \quad \text{Eqn 4}$$

where R ($\text{m}^3 \text{ atm mol}^{-1} \text{ K}^{-1}$) is the gas constant, T (K) is temperature, f is the mass fraction of PM that consists of absorbing organic material, and MW (g/mol) is the average molecular mass of the absorbing material.

2. Air Quality Modeling (AQM)

The use of computer models is an important component of investigations into atmospheric particle formation. Models, however, are -- by their very nature -- simplified representations of complicated natural phenomena, and may not accurately represent every chemical or physical process of interest. Sensitivity analyses of SOA modeling demonstrate that in both global (Tsigaridis & Kanakidou, 2003) and regional (Pun, et al., 2003) models, SOA predictions vary widely with different representations of the gas/particle partitioning process.

Numerous studies indicate that current air quality models underpredict ambient SOA levels (Heald, Ridley, Kreidenweiss, & Drury, 2010; Volkamer et al., 2006; Hodzic et al., 2009). Among the factors that have been discussed as contributing to modeled/measured discrepancies are uncertainties in: precursor emissions (Morris, et al., 2006); chemical mechanism features (Griffin, Dabdub, & Seinfeld, 2002); gas/particle partitioning processes (Kanakidou, et al., 2005); and relative humidity effects (Chang & Pankow, 2010). Addressing the shortcomings of AQMs involves requires, first, an explication of the standard SOA modeling framework.

2.1 SOA in AQMs

SOA yield, Y , is defined as the mass of SOA formed (M_o) per mass of hydrocarbon reacted (ΔHC). The aerosol yield of compound i , Y_i , was expressed by Odum (1996) as:

$$Y_i = M_o \sum_i \left(\frac{\alpha_i K_{p,om,i}}{1 + K_{p,om,i} M_o} \right) \quad \text{Eqn 5}$$

where α_i is a constant relating the fraction of reacting HC that is converted product, and $K_{p,om,i}$ is the equilibrium partitioning coefficient in terms of organic mass concentration ($K_{p,om,i} = K_{p,i} / f_{om}$).

Theoretically, one could sum this equation over all compounds present and determine total SOA yield. The sheer number of products formed by each SOA precursor, however, makes this nearly impossible (see e.g. Forstner, Flagan, & Seinfeld, 1997). It has become common practice to assume that each parent hydrocarbon forms only two products, one of high volatility, one of low volatility. This “two product” model has been shown to accurately reflect smog chamber yields (Odum, et al., 1996), and is widely implemented in AQMs.

In addition to the two-product assumption, most models simplify Eqn 4 by assuming that $\zeta=1$ (i.e., that mixing is thermodynamically ideal), and that OPM composition does not affect $\overline{MW}$ (Pankow, 2011). Most AQMs also do not account for the effect of water on SOA formation (Kanakidou, et al., 2005).

Simplifying Eqn 4 in this manner facilitates computational efficiency, but it neglects potentially important influences on partitioning behavior. Changing the mix of compounds present in PM will determine the chemical activity coefficients of individual species and the mean molecular weight of the absorbing phase. As shown in Eqn 4, this directly affects the partitioning constant K_p . Significant composition effects have been described by Bowman & Karamalegos (2002) and Pankow (2011), but have only recently begun to be accounted for in AQMs (Pun, Griffin, Seigneur, & Seinfeld, 2002). In

addition to general investigations into PM composition, there have been numerous studies evaluating the effects of water on OPM formation. Effects due to ambient humidity have been described in both modeling (e.g. Seinfeld et al., 2001; Chang & Pankow, 2010) and laboratory (e.g. Warren, Malloy, Yee, & Cocker, 2009; Zhou, et al., 2011) studies. This body of work indicates that AQMs using the two-product model with the assumption of ideality may be inadequately representing the gas/particle partitioning of organic compounds.

2.2 CMAQ

A widely used AQM is the Community Multiscale Air Quality (CMAQ) model (Zhang, Bocquet, Mallet, Seigneur, & Baklanov, 2012). CMAQ is a three-dimensional, gridded, regional model that simulates chemical reactions and transport of numerous atmospheric species. SOA processing occurs within the aerosol chemistry module of the CMAQ Chemistry-Transport Model (see Figure 3).

Figure 2-10. CMAQ chemistry-transport model and associated preprocessors

Figure 3. Overview of CMAQ processing functions

This aerosol module represents the particle size distribution (particle diameters from 0.001 to 10 μm) with three log-normally distributed modes: Aitken ($<0.1 \mu\text{m}$), accumulation (0.1 to 2.5 μm), and coarse (2.5 to 10 μm) (Binkowski & Shankar, 1995). The two interacting fine modes, taken together, represent $\text{PM}_{2.5}$. Aerosol processing in CMAQ takes into account nucleation, condensation, intermodal and intramodal coagulation, and wet and dry deposition. Figure 4 shows some details of PM in CMAQ; it should be noted that semivolatile organic compounds (SVOCs) are assumed to partition into organic aerosol, which is only represented in the accumulation mode portion of the size distribution.

Figure 4. Schematic of PM in CMAQ v4.7.1. Reproduced from Turner et al. (2011).

2.2.1 SOA module

CMAQ models SOA formation using an absorptive partitioning framework with a two-product fitting approach (Binkowski, 1999). CMAQ has provisions for allowing seven

gaseous precursors to undergo atmospheric oxidation, which can yield 12 semivolatile and 7 nonvolatile products (see Figure 5 and Figure A1.). Atmospheric reactions may be modeled using one of three available gas-phase chemistry mechanisms: RADM, CB4, or SAPRC99. These mechanisms simplify complex chemical reactions by lumping compounds based on either structure (CB4) or species (RADM and SAPRC99) type.

As shown in Figure 5, the six nonvolatile SOA species are formed in different manners. Three of them (ABNZ3, ATOL3, and AXYL3) result from the known ability of aromatic precursors to form nonvolatile SOA under low-NO_x conditions. One (ISO3) is due to acid-enhanced SOA formation from isoprene. The remaining two are lumped oligomer products: the SV anthropogenic and biogenic species are assumed to undergo condensed-phase accretion reactions, leading to AOLGA and AOLGB, respectively (see Carlton, et al., 2010 and references therein for details).

Gas-particle partitioning of the lumped products is implemented via Eqn. 8 of Schell (2001), which, rewritten in the notation used in this work is:

$$F_i = T_i - \frac{F_i/M_o}{K_p} \quad \text{Eqn 6}$$

Figure 5. Details of SOA processing in CMAQv4.7.1, reprinted from (Carlton, et al., 2010).

Table 1. Details of semivolatile products in CMAQv4.7.1.

gaseous precursor	α	SV product	SOA species	p°_L (atm)	K_p	MW (g/mol)	OM/OC	ΔH_{vap} (kJ/mol)
alkanes	0.072	SV_ALK	AALKJ	3.26E-12	50.0	150	1.56	40
benzene	0.094	SV_BNZ1	ABNZ1J	5.12E-11	3.3	144	2	18
	1.16	SV_BNZ2	ABNZ2	1.89E-08	9.0E-03	144	2	18
isoprene	0.23	SV_ISO1	AISO1J	2.95E-08	8.6E-03	96	1.6	40
	0.029	SV_ISO2	AISO2J	1.57E-10	1.6	96	1.6	40
sesquiterpenes	1.3	SV_SQT	ASQTJ	7.88E-10	0.08	378	2.1	40
high-yield aromatics	0.076	SV_TOL1	ATOL1J	3.38E-10	0.43	168	2	18
	0.15	SV_TOL2	ATOL2J	3.09E-09	4.7E-02	168	2	18
monoterpenes	0.11	SV_TRP1	ATRP1J	1.09E-09	0.13	168	1.4	40
	0.50	SV_TRP2	ATRP2J	1.61E-08	9.0E-03	168	1.4	40
low-yield aromatics	0.039	SV_XYL1	AXYL1J	1.67E-10	0.76	192	2	32
	0.11	SV_XYL2	AXYL2J	4.39E-09	2.9E-02	192	2	32

Table 2. Details of nonvolatile products in CMAQv4.7.1.

precursor	α	SOA species	MW (g/mol)	OM/OC
benzene	0.484	ABNZ3J	144	2
high-yield aromatics	0.471	ATOL3J	168	2
low-yield aromatics	0.373	AXYL3J	192	2
isoprene		AISO3J	162	2.7
Aged aerosol		AOLGAJ	176	2.1
		AOLGBJ	252	2.1

2.2.2 Current partitioning calculations

At each time step, the following input variables are used:

- T , the ambient temperature (K)
- P , the ambient pressure (atm)
- $\Delta\text{HC}_{j,t}$, the amount of VOC reacted during the time step(ppm)
- $\text{SVOC}_{i,t-1}$, the total (gas+particle) semivolatiles from the previous time step(ppm)
- POA, the primary organic aerosol present ($\mu\text{g}/\text{m}^3$)

The molecular weights of the gas-phase organic compounds and condensable products are denoted $\text{MW}_{\text{rog},j}$ and MW_i , respectively. The ideal gas law is used to convert the units of $\Delta\text{HC}_{j,t}$, and $\text{SVOC}_{i,t-1}$, as follows:

$$\text{totrog}_{j,t} = \frac{P * \text{MW}_{\text{rog},j}}{RT} * \Delta\text{HC}_{j,t} \quad \text{Eqn 7}$$

$$C_{\text{tot},i,t-1} = \frac{P * \text{MW}_i}{RT} * \text{SVOC}_{i,t-1} \quad \text{Eqn 8}$$

For each condensable compound i , the total (gas + particle, or $C_{gas,i,t} + C_{aer,i,t}$) concentration is found by adding the total amount from the preceding time step ($C_{tot,i,t-1}$) to the amount formed in the current one ($\alpha_i \cdot \text{totrog}_{j,t}$, where α is the mass-based stoichiometric coefficient). This total concentration is held constant throughout the partitioning calculations.

The mole fraction is found from

$$X_i = \frac{C_{aer,i,t}/MW_i}{\sum_{k=1}^{12} C_{aer,k,t}/MW_k + POA_t/MW_{POA}} \quad \text{Eqn 9}$$

The saturation concentration at the current temperature is found from the saturation concentration at 298 K using B_i , the preexponential constant of product i (Sheehan & Bowman, 2001) (note that $C^*=1/K_p$):

$$C_{sat,i}^* = C_{sat,i(298)}^* \cdot \frac{T}{298} \cdot \exp \left[B_i \left(\frac{1}{T} - \frac{1}{298} \right) \right] \quad \text{Eqn 10}$$

This effective saturation concentration is used in the following expression, which applies once thermodynamic equilibrium has been reached:

$$C_{gas,i,t} = C_{sat,i} = X_i C_{sat,i}^* \quad \text{Eqn 11}$$

The mass balance

$$C_{tot,i,t} = C_{gas,i,t} + C_{aer,i,t} \quad \text{Eqn 12}$$

may be combined with the preceding three equations, yielding the following expression for the particle-phase concentration of i (Schell, Ackerman, & Hass, 2001):

$$C_{aer,i,t} = C_{tot,i,t} - C_{sat,i}^* \frac{C_{aer,i,t}/MW_i}{\sum_{k=1}^{12} C_{aer,k,t}/MW_k + POA_t/MW_{POA}} \quad \text{Eqn 13}$$

It is this equation (corresponding to Eqn. 6) that governs modeled SVOC partitioning in CMAQ. While it accounts for the temperature dependence of K_p , it does not account for effects related to composition, relative humidity, and chemical activity.

3. Modeled-measured comparisons

3.1 Previous works

Tesche et al. (2006) concluded that CMAQ (v4.4) underestimates ambient summertime organic carbon by 65-91%. As part of a related evaluation of the performance of CMAQ, Morris et al. (Model sensitivity evaluation for organic carbon using two multi-pollutant air quality models that simulate regional haze in the southeastern United States, 2006) performed sensitivity analyses and found that the most likely explanation of this underestimation of OC was under prediction of SOA mass.. At the time of that study, CMAQ (v4.4) did not yet incorporate either oligomerization or SOA from BVOCs.

Yu (2007) used CMAQ v4.4 to predict organic carbon levels over the continental U.S. Comparisons with field measurements indicated that CMAQ was underpredicting secondary organic carbon (SOC) during the summer, especially in the southeast and central U.S. The magnitude of the error was up to approximately $0.5 \mu\text{g}/\text{m}^3$ in the southeast.

In 2008, an evaluation of the performance of CMAQ v4.5 over the eastern U.S. (Appel, Bhave, Gilliland, Sarwar, & Roselle, 2008) found similar summertime under-predictions in the southeast, with monthly average median biases for OC between 0.4 and $0.8 \mu\text{g}/\text{m}^3$.

Carlton (2010) described improved agreement between modeled and measured SOA mass due to the updates in SOA processing that were incorporated into CMAQ v4.7.1. The improvement, however, did not eliminate the summertime under-predictions

described above. Even in CMAQ v4.7.1, modeled OC levels were approximately 0.5 to 1.0 $\mu\text{g}/\text{m}^3$ below ambient levels during the summer in the Southeast U.S.

3.2 TOR vs TOT measurements

In order to evaluate AQM predictions of SOA, it is necessary to measure ambient SOC. In practice, though, there is no clear-cut way to differentiate between primary and secondary organic species in the atmosphere. Researchers generally use EC and OC measurements – sometimes combined with modeled parameters – to estimate SOC (Lee, Wang, & Russell, 2010).

Three main U.S. measurement systems provide EC and OC datasets:

- IMPROVE: Interagency Monitoring of Protected Visual Environments
- SEARCH: SouthEastern Aerosol Research and Characterization
- STN: Speciation Trends Network (U.S. Environmental Protection Agency)

Measurement stations from these three networks in the Eastern U.S. are shown in Figure 6.

Figure 6. Locations of measurement stations providing EC and OC data

IMPROVE and SEARCH stations measure carbon using thermal/optical reflectance (TOR), while STN stations use thermal/optical transmittance (TOT). The two methods produce comparable values of total carbon, but differ in the assignment of the OC/EC split, with TOT producing EC values that are 30-80% lower than values obtained via TOR (Chow, Watson, Chen, Arnott, & Moosmuller, 2004). Because the EPA's emissions inventories are based on the use of TOR for most source profiles (Yu, Dennis, Bhawe, & Eder, 2004), researchers have made differing decisions about whether to include STN measurements when comparing field data with their model results. Approaches include using only IMPROVE and SEARCH data (Yu, Dennis, Bhawe, & Eder, 2004; Yu, Bhawe, Dennis, & Mathur, 2007) and using all three data sets without correcting STN

measurements (Appel, Bhave, Gilliland, Sarwar, & Roselle, 2008; Morris, et al., 2006; Tesche, Morris, Tonnesen, McNally, Boylan, & Brewer, 2006).

This work follows the approach of Baek et al. (2011), which relied on an analysis by Cheng (2011), to convert values of EC and OC measured by TOT into (assumed) equivalent TOR values. Based on PM_{2.5} samples collected in the Southeast, Cheng determined conversion factors to go from EC_{TOT} to EC_{TOR} and from OC_{TOT} to OC_{TOR}. The following conversions were used in this work:

$$EC_{TOR} = EC_{TOT}/0.31$$

$$OC_{TOR} = OC_{TOT}/1.15$$

The resulting values of EC_{TOR} and OC_{TOR} were then combined with the IMPROVE and SEARCH measurements to create a set of OC observations, OC_{obs}.

Next, the method of Yu et al. (2007) was applied to calculate the secondary OC based on each {EC_{obs}, OC_{obs}} pair. This method utilizes the ratio of primary species OC_{pri}/EC_{pri}, which was found to average 2.46 (range 2.25 to 2.87) in the Southeast during summer.

$$OC_{sec} = OC_{obs} - \left[\min \left(OC_{obs}, \left(\frac{OC}{EC} \right)_{pri} * EC_{obs} \right) \right]$$

The resulting OC_{sec} is a semi-empirical value of SOC.

To obtain modeled SOC from CMAQ output (SOC_{mod}) each SOA species was divided by its OM/OC ratio and summed:

$$\begin{aligned}
SOC_{mod} = & \frac{1}{1.6}(AIS01J + AIS02J) + \frac{1}{1.4}(ATRP1J + ATRP2J) \\
& + \frac{1}{2.1}(ASQTJ + AOLGAJ + AOLGBJ) + \frac{1}{1.56}(AALKJ) \\
& + \frac{1}{2}(ATOL[1,2,3]J + AXYL[1,2,3]J + ABNZ[1,2,3]J + AORGCJ) \\
& + \frac{1}{2.7}(AIS03J)
\end{aligned}$$

SOC_{mod} can then be analyzed in terms of its overall levels and the contributions of the various secondary species, as well as compared with semi-empirical SOC values.

4. Modified Model

In this work, CMAQ has been modified in the following ways:

- Reasonable surrogate structures have been assigned to the 12 semivolatile and 6 nonvolatile OPM components
- The orgaer.F,v subroutine has been modified to:
 - use ambient relative humidity (RH) values to include water uptake in the SOA
 - calculate chemical activity coefficients
 - allow partitioning of SVOCs only into secondary condensed material (that is, eliminate POA from M_o).

4.1 Structures

Reasonable surrogate structures were chosen based on the CMAQ parameters shown in Tables 1 and 2, and other information provided in Carlton et al. (2010) and references therein. Details are provided in Tables 3 and 4.

4.2 Code modifications

The orgaer.F,v subroutine has been modified to call a subroutine that calculates partitioning based the method described by Pankow et al. (2001). This method explicitly includes water uptake by the aerosol, and calculates activity coefficients for water and all organic species using the UNIFAC method (described below). The computational algorithm utilizes a combination of golden section search and successive parabolic interpolation to find the solution for M_o , with the value of M_o at each step calculated

using an iterative method (Pankow, Seinfeld, Asher, & Erdakos, 2001). Therefore, the modified aerosol formation model accounts for the effects of mean molecular weight (MW), chemical activity (ζ), and relative humidity (RH) on K_p and the SOA formation.

4.3 UNIFAC

The approach that is most frequently used to estimate activity coefficients in organic mixtures (Marcolli & Peter, 2005) is application of the UNIversal quasi-chemical Functional-group Activity Coefficients (UNIFAC) method (Fredenslund, Jones, & Prausnitz, 1975). Rather than considering each of the many possible organic compounds separately, UNIFAC treats each compound as a collection of functional groups. By considering interactions among approximately 109 functional groups, UNIFAC can find the activity coefficient of each compound i based on the functional groups present in the compound itself and in the mixture in which it exists.

Saxena and Hildemann (1997) tested the ability of UNIFAC to predict water activity coefficients in several aqueous binary mixtures (and one aqueous ternary mixture) of multifunctional oxygenated organic compounds and found agreement with experimental data generally within 15%. Subsequent studies have provided further indications that UNIFAC is suitable for modeling organic aerosols (see e.g., Ansari & Pandis, 2000 and Seinfeld, Erdakos, Asher, & Pankow, 2001).

4.4 POA

Although CMAQ simply adds POA and SOA to determine M_o (see Figure 4 and Eqn 9), it is not necessarily true that primary and secondary OA will be miscible. Rather, it is

possible that the POA will be of low polarity and form a phase separate from the often high-polarity SOA (Erdakos & Pankow, 2004). Although box models have recently been developed to treat gas/particle partitioning into binary phase mixtures (Zuend, Marcolli, Peter, & Seinfeld, 2010), these approaches are too computationally intensive to be applied in a regional atmospheric model. For this study, the decision was made to assume that POA will form a separate condensed phase not available to the condensing organics. The CMAQ algorithms were thus modified so that M_o was equal to the sum of SV and NV secondary organic compounds only. This modified model has been designated CMAQ_s to emphasize that partitioning occurs only into secondary material.

Table 3. Details of chosen SV surrogate structures.

	Physical parameters					number of each UNIFAC group found in structure							formula
	p°_L (atm)	K_p	MW (g/mol)	OM/OC	nC	CH3 (1)	CH2 (2)	CH (3)	OH (15)	CH2CO (20)	CHO (21)	COOH (43)	
ALK	2.72E-12	50.0	180	2.14	7	2	2	2	3	0	0	1	C7H16O5
BNZ1	4.58E-11	3.3	161	2.68	6	0	0	0	0	1	1	2	C6H5O6
BNZ2	2.03E-08	9.0E-03	148	2.23	6	1	2	1	2	0	2	0	C6H12O4
ISO1	2.15E-08	8.6E-03	132	2.2	5	0	0	3	3	1	0	0	C5H8O4
ISO2	1.13E-10	1.6	133	2.23	5	0	0	5	4	0	0	0	C5H9O4
SQT	1.09E-09	0.08	273	1.52	15	5	4	0	0	2	2	0	C15H24O4
TOL1	3.49E-10	0.43	163	2.26	6	1	1	1	2	1	0	1	C6H11O5
TOL2	2.97E-09	4.7E-02	175	1.82	8	2	2	2	1	0	1	1	C8H15O4
TRP1	1.03E-09	0.13	177	1.84	8	2	2	2	3	1	0	0	C8H17O4
TRP2	1.37E-08	9.0E-03	198	1.83	9	0	1	1	0	2	3	0	C9H10O5
XYL1	1.85E-10	0.76	174	2.42	6	0	0	0	0	2	0	2	C6H6O6
XYL2	4.55E-09	2.9E-02	185	1.93	8	0	1	1	0	2	1	1	C8H9O5

Table 4. Details of chosen NV surrogate structures.

	Physical parameters					number of each UNIFAC group found in structure							formula
	p°_L (atm)	K_p	MW (g/mol)	OM/OC	nC	CH3 (1)	CH2 (2)	CH (3)	OH (15)	CH2CO (20)	CHO (21)	COOH (43)	
BNZ3	1.43E-14	9.7E03	180	3	5	0	0	3	3	0	0	2	C5H11O7
TOL3	5.39E-15	2.3E04	194	2.7	6	0	1	3	3	0	0	2	C6H10O7
XYL3	1.18E-13	2.0E04	218	2.3	8	0	1	4	1	0	0	3	C8H10O7
ISO3	2.32E-15	5.0E04	211	2.2	8	2	1	5	6	0	0	0	C8H19O6
OLGA	1.43E-14	8.3E03	206	2.5	7	0	2	2	1	0	0	3	C7H10O7
OLGB	7.58E-16	1.3E05	248	2.1	10	1	3	3	1	0	0	3	C10H16O7

4.5 Model runs

The emissions inventories obtained for use in this work were processed using the Sparse Matrix Operator Kernel Emissions (SMOKE) v. 2.5 software; the processing used the SAPRC07 lumped species gas-phase chemistry mechanism. The input consisted of the 2005 National Emissions Inventory (NEI), with adjustments as described by Zhang & Ying (2012).

Meteorology inputs were prepared by the Texas Commission on Environmental Quality.

Eleven days of simulations were run on a 36-km grid over the eastern U.S., with the first day discarded as spin-up time. The modeling domain is shown in Figure 7.

Figure 7. Domain used for model runs, overlaid by the 61 x 67 grid of 36km cells. The shaded box contains the area designated as Southeast US for this work.

A total of five versions of CMAQ were evaluated, as shown in Table 5. Unmodified CMAQ v.4.7.1 was run, as was CMAQ_s, the version modified to prevent partitioning into POA. Using the modified code described above, two partially modified versions were evaluated: mod_MW calculates the mean MW of the organics at each time step, while mod_MW_ufc also performs activity coefficient calculations using UNIFAC. The fully modified model, mod_MW_ufc_RH, in addition accesses meteorological humidity data and allows water to mix with the organic species.

Table 5. Details of CMAQ simulations.

Simulation name	Partitioning eqn	SV's partition into POA?	MW effect?	Activity effect?	Water uptake?	notes
CMAQ	Schell	Yes	--	--	--	Unmodified CMAQ
CMAQ_s	Schell	--	--	--	--	POA removed from M_o
Mod_MW	Pankow	--	Yes	--	--	
Mod_MW_ufc	Pankow	--	Yes	Yes	--	
Mod_MW_ufc_RH	Pankow	--	Yes	Yes	Yes	Fully modified case

4.6 Processing

Raw output from CMAQ consists of Network Common Data Form (netCDF) files. The Visualization Environment for Rich Data Interpretation (VERDI) program (www.verdi-tool.org) was used for initial processing of the CMAQ output. VERDI was used to create plots directly, and to output shapefiles for use in the Geographic Information System mapping application ArcGIS.

Point values of measured EC and OC were downloaded from Colorado State University's VIEWS site (<http://views.cira.colostate.edu/web/>). These values were processed as described in section 3.2. The latitude and longitude values of the measurement stations were then used to plot this point data in ArcGIS 10.0. The spatial join function in ArcGIS enabled pairing of modeled and measured SOC.

5. Results and Discussion

5.1 Computational efficiency

Table 6 shows that the modified model took approximately ten times as long as the unmodified to run. This varied significantly, with the average time needed to simulate one day ranging from 23 to 42 minutes. The model took longer to run at higher atmospheric RH levels.

Table 6. Comparison of computation times

	CMAQ	CMAQ_mod
# of processes	96 (12 nodes)	96 (12 nodes)
Avg minutes to simulate one day	3	31

5.2 Spatially averaged SOC

Figure 8 plots the average SOC over an area covering columns 25 to 60 and rows 15 to 45 (see Figure 7). This area was chosen to represent the bulk of the Southeastern US; relationships among model cases shown here are typical of those observed over various other sub-domains.

5.2.1 CMAQ_s As expected, when POA is removed from M_o , the total SOA formation decreases due to the reduction in absorbing material. Over the Southeast, the difference in hourly SOC between the CMAQ and CMAQ_s cases ranges from 0.07 to 0.17 $\mu\text{g}/\text{m}^3$. (Note that these values correspond to differences in total SOA ranging from 0.13 to 0.30 $\mu\text{g}/\text{m}^3$. Although the overall OM/OC ratio varies with SOA composition, it is reasonable to convert all the SOC values in this section by assuming $\text{SOA} \approx 1.8 * \text{SOC}$.) The average

decrease in SOC over the model run is $0.12 \mu\text{g}/\text{m}^3$, a reduction of 57% due to removal of POA.

Figure 8. Time series of SOC, averaged over cells (25,15) to (60,45)

5.2.2 mod_MW and mod_MW_ufc When the mean molecular weight of the organic material is accounted for in the partitioning calculations (mod_MW), the modeled SOC decreases further, averaging $0.05 \mu\text{g}/\text{m}^3$ lower than the CMAQ_s case, a reduction of approximately 28%. Including the effect of activity (mod_MW_ufc), results in a further reduction of SOA formation, an average of $0.05 \mu\text{g}/\text{m}^3$ less than in mod_MW, representing a 31% decrease. This indicates that the component activity coefficients have

increased ($\zeta_i > 1$), leading to a reduction in K_p for enough compounds that SOA decreases.

5.2.3 mod_MW_ufc_RH Once the effects of water *and* molecular weight are accounted for, however, increases in the SOA formation are observed. Taking CMAQ_s as the base case, the fully modified scenario (mod_MW_ufc_RH) produced increases in SOC ranging from 0.09 to 0.25, and averaging $0.14 \mu\text{g}/\text{m}^3$ (a 66% increase). This is the most appropriate comparison, as these scenarios are both based on SVOCs partitioning into secondary compounds only. Even when compared with unmodified CMAQ, however, the fully modified case generally increased SOC (by up to $0.12 \mu\text{g}/\text{m}^3$) with occasional decreases. On average, the fully modified model increased SOC by 9% when compared with unmodified CMAQ.

5.3 Temporally averaged SOC

As discussed above, the fully modified model produced more SOC than the CMAQ_s base case. Figure 9 shows the average SOC over the 10-day model run; for the CMAQ_s case, the highest average SOC in any grid cell was $1.11 \mu\text{g}/\text{m}^3$; in the fully modified case, it was $1.57 \mu\text{g}/\text{m}^3$.

Figure 9. Maps of SOC (averaged over 10-days) from CMAQ_s (left) and CMAQ_{mod} (right).

The absolute difference in SOC, as an average over the 10-day model run, ranged from -0.04 to $0.58 \mu\text{g}/\text{m}^3$; this is plotted in Figure 10. The ratio $\text{SOC}_{\text{mod}} / \text{SOC}_{\text{CMAQ}_s}$ ranged from 1.06 to 4.46 and is shown in Figure 11.

Figure 10. Map of absolute difference ($\mu\text{g}/\text{m}^3$) between CMAQ_mod and CMAQ_s.

Figure 11. Map of the ratio of $\text{SOC}_{\text{mod}} / \text{SOC}_{\text{CMAQ}_s}$

5.4 Speciation

In both the base case and modified CMAQ runs, SOC was dominated by contributions from biogenic species. The biogenic species and their oligomers together constituted an average of 80% and 84% of the total SOC in the base and modified cases, respectively (see Figure 12). The large impact on SOC of the biogenic fraction is consistent with previous studies (e.g., Kleindienst, et al., 2007; Ding, Zheng, Edgerton, Jansen, & Wang, 2008). In the CMAQ_s runs, SOC was dominated by contributions from three species: ATRP1, ASQT, and AOLGB, which contributed an average of 62% of the total SOC (see Figure 14a).

Figure 13 shows the difference between the base (CMAQ_s) and modified (mod_MW_ufc_RH) cases in terms of six general types of SOA: anthropogenic and biogenic semivolatile, nonvolatile, and oligomer species. All categories of compounds can be seen to increase in the modified model; the largest increases – relative to the base-case SOA level – were observed in NV biogenics (average increase of 139%), while the smallest occurred in the anthropogenic oligomers (average increase of 22%).

Examination of Figure 15 reveals that these changes were largely driven by increases in two species -- ATRP1 and AISO2 -- and somewhat offset by large decreases in ASQT. (AOLGB also experiences significant increases, as would be expected to result from increases in its predecessor compounds.)

(For simplicity, mod_MW_ufc_RH is designated “mod” in many of the figures that follow. This always refers to the fully modified case.)

Figure 12. Aerosol prevalence by type: (a) CMAQ partitioning into semivolatiles only, and (b) fully-modified model. Types of aerosol are anthropogenic and biogenic oligomers, nonvolatile, and semivolatile species.

Figure 13. Difference between CMAQ_mod and CMAQ_s, in terms of contributions to SOC from all secondary OPM types, as defined in Figure 12. “Net change” plots the difference in total SOC.

Figure 14. Aerosol prevalence by species: (a) CMAQ partitioning into semivolatiles only, and (b) fully-modified model.

Figure 15. Difference between modified case and CMAQ_s, in terms of contributions to SOC from all species.

Figure 16 shows typical values of ζ_i calculated by CMAQ_mod. During the sixth hour of Day 10, in a cell with RH=52%, activity coefficients ranged from 0.53 (ISO1) to 7.68 (SQT). In a cell with RH=84%, the range was 0.26 (ISO3) to 16.1 (SQT). This shows that SQT was the most hydrophobic of the products, and referring to Figure 15, as expected, was also the species that experienced the largest decrease in mass fraction in the particulate phase.

The high ζ_{SQT} values found here indicate that SQT is being driven out of the secondary PM. In CMAQ_mod, this means that it does not contribute to OPM levels. But it is not necessarily true that this would occur; with reference to the issue of phase separation discussed in section 4.4, it is possible that conditions in the nonpolar organic phase would be more favorable, leading to SQT condensing into the POA compartment. In fact, using POA and RH values from Day 10, hour 6, and assigning POA structures as described in Chang & Pankow (2010), UNIFAC-calculated ζ_{SQT} values range from 1.54 to 2.02.

Figure 16. Activity coefficients of SOA species at three relative humidity levels. Values are taken from three grid cells during Hour 6 of JD 250

5.5 Sensitivity of partitioning

Previous theoretical studies of SOA formation have predicted that low M_o levels are more sensitive to perturbations in system parameters such as relative humidity (Pankow & Chang, 2008; Pankow, 2013). That prediction is supported by these model results. Figure 17 plots the ratio of SOC formed in CMAQ_mod to that formed in CMAQ_s. On the x-axis is the SOC mass from the CMAQ_s run. The largest increases (up to 11 times as much SOC) are seen in the cells where there was little SOC formed originally. In contrast, when SOC levels were originally high, there was little difference between SOC in CMAQ_mod and CMAQ_s.

Figure 17. Ratio vs base-case SOC, symbolized by relative humidity. Values shown are from JD 246 over the southeastern US.

This relationship is also demonstrated in Figure 18. Here the SOC ratio is plotted against the ambient relative humidity. Again, the high modified/base ratios are observed where SOC levels were low.

Figure 18. Ratio vs relative humidity, symbolized by SOC_{CMAQ_s}. Values shown are from JD 246 over the southeastern US.

5.6 Modeled vs. measured SOC

5.6.1 Southeast US

While the preceding analysis has compared CMAQ_mod with CMAQ_s, it was also found that CMAQ_mod produced increased SOA formation even relative to unmodified CMAQ (see Figure 8). That is, even though the modified model does not partition into POA – so there is less mass available – the effects of water are large enough to lead to an overall increase in SOA formation. In this section, CMAQ_mod output is compared with field measurements to determine if the known underpredictions of unmodified CMAQ have been improved.

461 measurements (from the three networks described in section 3.2) were paired with corresponding modeled values. Mean fractional bias (FB) and fractional error (FE) were calculated as (Boylan & Russell, 2006):

$$FB = \frac{1}{N} \sum_{k=1}^N \frac{SOC_{CMAQ,k} - SOC_{obs,k}}{0.5(SOC_{CMAQ,k} + SOC_{obs,k})}$$

$$FE = \frac{1}{N} \sum_{k=1}^N \frac{|SOC_{CMAQ,k} - SOC_{obs,k}|}{0.5(SOC_{CMAQ,k} + SOC_{obs,k})}$$

As shown in Table 7, the modified model decreased the magnitudes of both FB and FE by about 12% and 10%, respectively, for SOC, while having little impact on EC and OC predictions.

Table 7. Comparison of mean fractional bias and fractional error between unmodified CMAQ and full modified model.

	FB (%)		FE (%)	
	CMAQ	CMAQ_mod	CMAQ	CMAQ_mod
EC	-37	-38	58	59
OC	-87	-85	99	97
SOC	-114	-102	133	123

5.6.2 SEARCH sites

The eight stations in the SEARCH network (see Figure 6) have the largest number of measurements per site: data is acquired daily, rather than every three days as for the IMPROVE and STN sites. Furthermore, the SEARCH sites consist of rural/urban pairs, as shown in Figure 19.

Figure 19. Location and type of SEARCH sites.

When FB_{SOC} and FE_{SOC} at the individual SEARCH sites are evaluated, the largest fractional errors in unmodified CMAQ are seen at the four urban sites (grouped together on the left half of Figure 20b). The fully modified model nearly halves the FE values of BHM and JST –the stations within the largest urban areas -- while slightly decreasing those of GFP and PNS (as well as all of the rural sites).

Figure 20. Comparison (between unmodified CMAQ and CMAQ_mod of fractional bias and fractional error in predictions of SOC.

5.6.3 Overall model accuracy

Figure 21 shows an example of the daily average SOC and its relation to the available SOC measurements. While this daily average SOC is from a CMAQ_mod run, unmodified CMAQ produces quite similar results. CMAQ's known SOC underpredictions are visually evident in both cases.

As described in section 5.4, some of this underprediction would likely be remedied by allowing partitioning into POA when appropriate. With respect to SQT only, CMAQ_mod produces an average of $0.06 \mu\text{g}/\text{m}^3$ less SOC than unmodified CMAQ due to unfavorable activities in the SOA mixture.

September 5,
2006

SOC
 $\mu\text{g}/\text{m}^3$

Figure 21. Julian Day 248, 2006: modeled SOC_{mod} , overlaid with semi-empirical SOC_{obs} values calculated from SEARCH, IMPROVE, and STN measurements

6 Conclusions

A series of runs of a regional air quality model, CMAQ v. 4.7.1, were performed, using an improved method of calculating gas/particle partitioning. This method utilizes ambient relative humidity and incorporates iterative calculations of molecular weight and activity in order to more accurately represent the processes governing SOA formation. The results suggest that agreement between model-predicted levels of SOA and field measurements may be improved somewhat with more accurate gas/particle partitioning calculations, although significant discrepancies remain.

As expected, the largest impacts were observed in areas with low SOA levels, demonstrating that these areas are particularly sensitive to the effect of water and non-ideality on SOA formation. In addition, the effects found in this work may be particularly important in urban areas, as reflected in the SEARCH station values; further study of the underlying processes is necessary to determine if the findings of this work are generalizable in this respect. Finally, the issue of phase separation in organic aerosols is an important component that has yet to be implemented in regional air quality models.

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