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Molecular View Modeling of Atmospheric Organic Particulate Matter: Incorporating Molecular Structure and Co-Condensation of Water

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45 **ABSTRACT**

46 Most urban and regional models used to predict levels of organic particulate matter (OPM) are
47 based on fundamental equations for gas/particle partitioning, but make the highly simplifying,
48 anonymized-view (AV) assumptions that OPM levels are not affected by either: a) the molecular
49 characteristics of the condensing organic compounds (other than simple volatility); or b) co-
50 condensation of water as driven by non-zero relative humidity (RH) values. The simplifying
51 assumptions have allowed parameterized chamber results for formation of secondary organic
52 aerosol (SOA) (e.g., “two-product” (2p) coefficients) to be incorporated in chemical transport
53 models. However, a return towards a less simplistic (and more computationally demanding)
54 molecular view (MV) is needed that acknowledges that atmospheric OPM is a mixture of organic
55 compounds with differing polarities, water, and in some cases dissolved salts. The higher
56 computational cost of MV modeling results from a need for iterative calculations of the
57 composition-dependent gas/particle partition coefficient values. MV modeling of OPM that
58 considered water uptake (but not dissolved salts) was carried out for the southeast United States
59 for the period August 29 through September 7, 2006. Three model variants were used at three
60 universities: CMAQ-RH-2p (at PSU), UCD/CIT-RH-2p (at UCD), and CMAQ-RH-MCM (at
61 TAMU). With the first two, MV structural characteristics (carbon number and numbers of
62 functional groups) were assigned to each of the 2p products used in CMAQv.4.7.1 such that
63 resulting predicted $K_{p,i}$ values matched those in CMAQv.4.7.1. When water uptake was allowed,
64 most runs assumed that uptake occurred only into the SOA portion, and imposed immiscibility of
65 SOA with primary organic aerosol (POA). (POA is often viewed as rather non-polar, while SOA
66 is commonly viewed as moderately-to-rather polar. Some runs with UCD/CIT-RH-2p were used
67 to investigate the effects of POA/SOA miscibility.) CMAQ-RH-MCM used MCM to generate
68 oxidation products, and assumed miscibility of SOA and POA. In a ~500 km wide band from

69 Louisiana through to at least North Carolina, CMAQ-RH-2p and UCD/CIT-RH-2p predicted that
70 water uptake can increase SOA levels by as much as 50 to 100% (from a range of ~ 1 to $2 \mu\text{g m}^{-3}$
71 to a range of ~ 1 to $4 \mu\text{g m}^{-3}$). CMAQ-RH-MCM predicted much lower effects of water uptake
72 on SOA levels ($<10\%$ increase). The results from CMAQ-RH-2p and UCD/CIT-RH-2p are
73 considered more reflective of reality. In the Alabama/Georgia hotspot, both CMAQ-RH-2p and
74 UCD/CIT-RH-2p predicted aerosol water levels that are up to nearly half the predicted SOA
75 levels, namely ~ 0.5 to $2 \mu\text{g m}^{-3}$. Such water levels in SOA will affect particle optical properties,
76 viscosity, gas/particle partitioning times, and rates of hydrolysis and water elimination reactions.

77

78 **Keywords:** organic particulate matter, OPM, organic aerosol, OA, secondary organic aerosol,
79 SOA, absorption model, RH effects, water, co-condensation of water

80

81 ■ INTRODUCTION

82 Most current 3D chemical transport models use primitive approaches for predicting levels of
83 organic particulate matter (OPM) in the atmosphere: they incorporate only the barest aspects of
84 the chemistry of the complex mixes of organic compounds that may occur, ignore the role of co-
85 condensing water, and usually do not attempt to consider the time-dependent oxidation reactions
86 that continually transform organic compounds in the atmosphere. This is problematic: 1) aerosol
87 particles are known to have direct and indirect effects on climate (Ramanathan et al., 2001;
88 Kanakidou et al., 2005); 2) ambient levels of fine PM are associated with increases in human
89 morbidity and mortality (Pope and Dockery, 2006); and 3) atmospheric PM is often 20 to 60%
90 organic material (Kanakidou et al., 2005). In those contexts, the composition of the OPM can
91 strongly affect light absorption (Andreae and Gelencsér, 2006; Updyke et al. 2012; and Song et
92 al., 2013), cloud condensation (Petters and Kreidenweis, 2007), and particle deposition rates
93 (composition affects hygroscopicity (Petters and Kreidenweis, 2007) and hygroscopicity affects
94 deposition rates (Vong et al., 2010)).

95 While views vary regarding the advantages and deficiencies of different modeling
96 approaches, there is scientific consensus at least that in the general case: 1) a portion of ambient
97 OPM has some volatility, and so is in active evaporation/condensation (*i.e.*, gas/particle)
98 exchange with the gas phase; and 2) a second portion is essentially non-volatile at the ambient
99 temperature T . Both the exchanging and non-volatile fractions can be subdivided as
100 anthropogenic or biogenic, and further as primary (directly emitted) or secondary. For a neutral
101 species, an inherently low volatility is always ascribable to the combined effects of molecular
102 weight (MW), polarity, and temperature T . Temperature plays its role through vapor pressure,
103 which sets the volatility for every particular pure liquid compound i . Atmospheric OPM,
104 however, is never a single pure compound, so the effective volatility of each constituent

105 compound is lowered by dilution, and changed by non-ideal solution effects (Pankow, 1994a).
106 Regarding acidic and basic species i.e. organic carboxylic acids can be deprotonated to form
107 carboxalate ions, and organic amines can be protonated to form aminium ions, charge alone is
108 enough to prevent volatilization at ambient T values (*cf.* protonation of ammonia to form
109 ammonium ion) (Pankow, 2003).

110 Chemical transport models in current use for atmospheric OPM modeling such as CMAQ
111 and PMCAMx (Carlton et al., 2010; Robinson et al., 2007) suffer from two deficiencies that
112 affect OPM predictions. *First*, they both utilize a severely *anonymized view* (AV) in which a
113 limited number (20 or less) of “hypothetical lumped compounds” is invoked. The “compounds”
114 vary only by inherent volatility, with no other characteristics such as polarity. Examples of the
115 AV approach include the two-product (2p) view of Odum et al. (1996, 1997) as used in CMAQ
116 (Carlton et al., 2010), and the 1-D volatility basis set (VBS) of Donahue et al. (2006). In fact,
117 contrary to the AV assumption, both low polarity and polar constituents are always present in
118 atmospheric OPM, and those differences will affect the levels and properties of the OPM. Low
119 polarity constituents include plant wax materials, cooking oils, and petroleum hydrocarbons
120 (Schauer et al., 1999; Schauer et al., 2002; Conte and Weber, 2002); polar constituents include
121 secondary compounds with functional groups such as hydroxyl and carboxyl (e.g., Yu et al.,
122 1999; Zhang et al., 2007). Each OPM phase will therefore be a mix with a mixture-average
123 polarity that is between non-polar and highly polar. For each exchanging compound i , the
124 gas/particle partitioning is affected by the polarity match or mismatch in the liquid between the
125 compound and the OPM mixture. A high mismatch (relative to condensation into a liquid in
126 which $\zeta_i = 1$) causes $\zeta_i > 1$ which reduces the condensation tendency (*viz.* increases the
127 volatility) (Pankow, 1994a; Pankow, 2003). When the condensed material includes both non-
128 polar and rather polar compounds in similar abundance, phase separation in the OPM becomes

129 certain (Erdakos and Pankow, 2004; Zuend et al., 2010; Donahue et al., 2011), as when within
130 the miscibility gap of a partially miscible binary system. While anonymized models ignore these
131 complexities, a *molecular view* (MV) can assign functionalities to each OPM compound to allow
132 consideration of non-ideality effects, and phase separation.

133 *Second*, AV modeling precludes consideration of water uptake: there is no character of
134 the OPM that can be used to estimate hygroscopicity. However, theory (e.g., Pankow, 1994a;
135 Pankow, 2010; Pankow and Chang, 2008; Chang and Pankow, 2010), and applications with the
136 3D sesqui-MADRID model (Pun, 2008), predict that important effects on OPM levels are
137 possible. Indeed, although water is far more volatile than “condensable” organic compounds, it
138 is also always vastly more abundant in the atmosphere than the sum of all condensable organic
139 compounds ($\sim 10^7 \mu\text{g}/\text{m}^3$ water at 20 °C, 50% relative humidity (RH), and 1 atm total pressure).
140 In addition to the importance of the effects of water on OPM levels and that of hygroscopicity
141 itself (e.g., Massoli et al., 2010, Duplissy et al. 2011), there are expected significant effects of
142 absorbed water on viscosity (Iwata and Shimada, 2013) and thus gas/particle equilibration times
143 (Shiraiwa et al., 2011; Bones et al., 2012), and reaction rates within organic liquids (Vollhardt
144 and Schore, 2007). Fortunately, once an adequately flexible MV model is built for considering
145 compounds with varying polarity and molecular weight, inclusion of water as a fully-interacting
146 partitioning compound is simple. With the 2-D VBS of Donahue et al. (2011), while some
147 measure of MV effects amongst the partitioning organic compounds can be considered, only O:C
148 ratio and carbon number are available as measures of molecular variability, and water is not
149 included in the basis set so it cannot be predicted to be present in, or have an effect on the levels
150 of, the modeled OPM. We are interested in modeling carried out considering specific
151 functionalities (alcohol groups, aldehyde groups, carboxylic acid groups, etc.) assigned to
152 partitioning organic molecules, and allowing water uptake.

153 Herein we provide an overview of the OPM model development required for a simple
 154 consideration of MV effects for non-ionic organic compounds, with water uptake into a single
 155 OPM phase; the effects of ionization and multiple OPM phases (i.e., phase separation) are
 156 beyond the scope of this work. Simulations are described for the southeast United States for the
 157 period August 29 through September 7, 2006 using three chemical transport models modified to
 158 include MV features for OPM calculations. The implications of water uptake for OPM phase
 159 characteristics are considered.

160 ■ EQUILIBRIUM GAS/PARTICLE PARTITIONING - EQUATIONS AND SOLUTIONS

161 **General.** The gas/particle partitioning constant for compound i is defined

$$162 \quad K_{p,i} \text{ (m}^3 \text{ }\mu\text{g}^{-1}\text{)} = \frac{c_{p,i}}{c_{g,i}} \quad (\equiv 1/C_i^*) \quad (1)$$

163 where $c_{p,i}$ ($\mu\text{g }\mu\text{g}^{-1}$) is the concentration within the particle phase, and $c_{g,i}$ ($\mu\text{g m}^{-3}$) ($\equiv A_i$) is the
 164 concentration in the gas phase. In the 1-D “volatility basis set” (VBS) approach of Donahue et
 165 al. (2006), $K_{p,i}$ is manifested in terms of the saturation concentration C_i^* ($\mu\text{g m}^{-3}$). If the total
 166 mass concentration of the absorbing phase is M ($\mu\text{g m}^{-3}$), and F_i ($\mu\text{g m}^{-3}$) is the particle-
 167 associated concentration of i for the aerosol system, then (Pankow, 1994a)

$$168 \quad K_{p,i} \text{ (m}^3 \text{ }\mu\text{g}^{-1}\text{)} = \frac{F_i/M}{A_i} \quad (2)$$

$$169 \quad F_i = K_{p,i} M A_i \quad (3)$$

170 As usual, let T_i ($\mu\text{g m}^{-3}$) = $A_i + F_i$ be the total (i.e., gas+particle) concentration of i , and the
 171 fraction of i in the particle phase is

$$172 \quad f_{p,i} \equiv \frac{F_i}{F_i + A_i} = \frac{K_{p,i} M}{1 + K_{p,i} M} \quad (4)$$

$$173 \quad M = \sum_i F_i = \sum_i f_{p,i} T_i = \sum_i \frac{K_{p,i} M}{1 + K_{p,i} M} T_i \quad (5)$$

174
$$1 - \sum_i \frac{K_{p,i} T_i}{1 + K_{p,i} M} = 0 \quad (6)$$

175 When water is considered, M includes a contribution from water because F_w is one of the F_i , and
 176 M here equals M_{0+w} as used elsewhere (Pankow, 2010). In the case of some essentially non-
 177 volatile component i , the value of $K_{p,i}$ is very large so that $f_{p,i} = 1.0$.

178 For $M > 0$, the function represented by the left hand side of Eq.(6) is a smooth sigmoidal
 179 curve. As M increases from 0, the curve varies from $(1 - \sum_i K_{p,i} T_i)$ to 1. If $\sum_i K_{p,i} T_i > 1$, then
 180 the function will be negative at very small M , and there will be an easily found zero crossing
 181 (i.e., a solution), which gives the condition at which the multi-component system is saturated in
 182 the gas phase with material left over for $M > 0$. With $K_{p,i}$ as the inverse of the saturation
 183 concentration C_i^* , for a single component system $K_{p,1} T_1$ gives the ratio between the total and
 184 saturation concentrations, so that $M > 0$ only when $K_{p,1} T_1 > 1$.

185 **Mathematical Solution in the Anonymized View (AV).** In AV models of OPM, at a
 186 particular value of T , the $K_{p,i}$ values are fixed and not dependent on OPM composition. As
 187 noted, associated options include: a) the 2p model of Odum et al. (1996, 1997) for condensation
 188 of “secondary” organic aerosol (SOA) compounds; and b) the 1-D-VBS approach of Donahue et
 189 al. (2006) for general OPM modeling. Given input sets of T_i and the associated $K_{p,i}$, a root
 190 solver with Eq.(6) can find the root value of M such that the left hand side equals zero. The root
 191 value of M can then be used to calculate each F_i by Eq.(3). CMAQv.4.7.1 uses this approach
 192 with 2p values of $K_{p,i}$ (chamber-derived) for assumed oxidation products of several SOA parent
 193 hydrocarbons. Note that: a) low values of the T_i and/or $K_{p,i}$ can cause there to be no real positive
 194 root value for M in Eq.(6), in which case $M = 0$; but b) if $T_i > 0$ for any species considered to be
 195 non-volatile, $M > 0$ regardless of the values of the other T_i and $K_{p,i}$.

196 **Mathematical Solution in the Molecular View (MV).** The MV approach is needed because
 197 $K_{p,i}$ values depend on OPM composition. For absorptive partitioning into liquid OPM (Pankow,
 198 1994a):

$$199 \quad K_{p,i} = \frac{RT}{10^6 \overline{MW} \zeta_i p_{L,i}^{\circ}} \quad (7)$$

200 where: R = gas constant ($8.2 \times 10^{-5} \text{ m}^3 \text{ atm mol}^{-1} \text{ K}^{-1}$); \overline{MW} (g mol^{-1}) = mole-average mole-
 201 cular weight of the absorbing OPM phase; ζ_i (dimensionless) = mole-fraction scale activity
 202 coefficient; and $p_{L,i}^{\circ}$ (atm) = vapor pressure at temperature T (K) of pure liquid i . (The factor 10^6
 203 is a conversion factor that gives the number of μg per gram.) For reference, if the OPM were
 204 pure liquid i , then $\overline{MW} = MW_i$, $\zeta_i = 1$, $c_{p,i} = 1$, and C_i^* gives the gas-phase saturation
 205 concentration in equilibrium with the pure liquid.

206 The compositional dependence of $K_{p,i}$ is caused by variability in: a) ζ_i , which accounts
 207 for the comfort match/mismatch between i in *its own liquid self* vs. in *the OPM*, as due to
 208 differences in characteristics such as polarity and size; and b) \overline{MW} , which accounts for the
 209 colligative consequences of $MW_i \neq \overline{MW}$. Because of the low MW of water (18 g mol^{-1}), water
 210 absorption by OPM can cause marked reductions in \overline{MW} , which can cause every $K_{p,i}$ to
 211 increase. For example, absorption by dry OPM with $\overline{MW} = 200 \text{ g mol}^{-1}$ of 2% by weight water
 212 lowers \overline{MW} to 167 g mol^{-1} , tending to cause all $K_{p,i}$ values to increase by 20%. When OPM
 213 levels are low and most of the potentially condensable organic material is in the gas phase, the
 214 predicted OPM level at equilibrium is very sensitive to even relatively minor changes in the $K_{p,i}$
 215 and T_i values (Pankow, 2010, 2013).

216 In an MV modeling approach, the partitioning compounds have differentiating structural
 217 features, and the equilibrium composition can only be obtained by the coupled iterative solution

218 of Eq.(7) for all i together with Eq.(6) (Pankow, 1994b). A $K_{p,i}$ algorithm first takes guess values
219 of F_i (*i.e.*, the OPM guess composition) to compute the corresponding guess values of all the ζ_i
220 and \overline{MW} , and thus the $K_{p,i}$ values for that composition based on Eq.(7). As discussed above, if
221 $\sum_i K_{p,i} T_i > 1$, an OPM root solver with Eq.(6) can use the $K_{p,i}$ values and the guess $M (= \sum_i F_i)$ to
222 easily obtain a new M , which can be used with Eq.(4) to obtain the new F_i . Iterative alternation
223 between the $K_{p,i}$ algorithm and the OPM root solver continues until convergence is obtained (as
224 evaluated by examination of either: 1) the $K_{p,i}$; or 2) the F_i). When phase separation is not being
225 considered, we have not experienced difficulties obtaining convergence because of local minima.
226 Oscillation during the alternation between the two solutions may occur at low OPM levels, but is
227 increasingly dampened when “non-volatile” components contribute significantly, and/or
228 predicted OPM levels are large relative to the condensable mass: the mathematical sensitivity is
229 dampened as each particular $T_i > 0$ is consigned to the OPM phase (common in current
230 modeling), and when M is large relative to the condensable mass (Pankow, 2013).

231 ■ METHODS: THREE MOLECULAR VIEW-ENABLED MODELS

232 **Models.** Table 1 summarizes details of the three chemical transport models used here for
233 MV consideration of OPM levels; all consider water uptake into OPM. For each: 1) an iterative
234 solution was begun at each point in the x,y,z,t domain using the $K_{p,i}$ algorithm with the local RH
235 and T , guess values of the F_i , and the UNIFAC model (Fredenslund et al., 1977), to calculate
236 corresponding guess of ζ_i and \overline{MW} and the resulting $K_{p,i}$; 2) the $K_{p,i}$ are passed to an OPM root
237 solver; 3) iteration proceeds until convergence is reached. CMAQ-RH-2p was derived from
238 CMAQv.4.7.1 (an AV model) by addition of two features: a) $K_{p,i}$ algorithm; and b) an input ar-
239 ray (for each 2p product) for values of the numbers of particular functional groups and the MW.
240 The values for the MV characteristics array for each product (summarized in Table 2) were ob-

241 tained along with the carbon number n_c using the approach of Chang and Pankow (2010) such
242 that the utilized values of MW_i and $p_{L,i}^o$ ($T = 298$ K, by SIMPOL.1 (Pankow and Asher, 2008))
243 for the product gave a $(K_{p,i})^{-1}$ value that closely matches the C_i^* value used in CMAQv.4.7.1.
244 UCD/CIT-RH-2p employs the two features and corresponding code that CMAQ-RH-2p adds to
245 CMAQv.4.7.1, but is otherwise based on the UCD/CIT model (Kleeman et al., 2001; Ying et al.,
246 2008). UCD/CIT uses an updated secondary organic aerosol module based on CMAQv.4.7.1,
247 but does not consider SOA production by in-cloud processes. CMAQ-RH-MCM is based on
248 MCM-SOA (Li et al., 2015), but adds water uptake into the OPM (MCM-SOA provided the first
249 adaptation of CMAQ for MV consideration of SOA formation using a $K_{p,i}$ algorithm, employing
250 UNIFAC for the latter). MCM-SOA uses the near-explicit chemical reaction model MCM.3.2
251 (Jenkin et al., 2012) to produce oxidation products available for condensation of SOA. For each
252 time step, values are initialized using the values produced by the preceding step. None of the
253 models considered partitioning to mostly-water phases, so Henry's Law partition coefficients for
254 water were not used. For all three models, the spatial resolution was 36 km; operator splitting
255 time steps were between 6 and 10 min.

256 **Runs.** Averaged model output for the southeast United States was obtained for the 10
257 day period August 29 through September 7, 2006, with 1 to 5 *preceding* days of model "spin-
258 up". For each model, the base (B) case run assumed no water uptake by the OPM; for each
259 model water (W) mode run was also carried out, with water uptake allowed into the SOA as
260 determined at each point (x,y,z,t) according to the local conditions. All runs with CMAQ-RH-2p
261 imposed immiscibility of SOA with primary organic aerosol (POA) (POA is often viewed as
262 rather non-polar, while SOA is commonly viewed as moderately-to-rather polar); CMAQv.4.7.1
263 assumes POA/SOA miscibility. When water uptake was allowed in CMAQ-RH-2p, it was

264 assumed that uptake occurred only into the SOA portion. UCD/CIT-RH-2p was executed
265 similarly, except that some runs allowed POA/SOA miscibility with water uptake into the
266 mixture. CMAQ-RH-MCM assumes POA/SOA miscibility with water uptake into the mixture.

267 ■ RESULTS AND DISCUSSION

268 Model results are presented in Figures 1 and 2. In Figure 1, the first and second (a and
269 b) panel columns indicate that both CMAQ-RH-2p and UCD/CIT-RH-2p predict that water
270 uptake can significantly increase average SOA levels in areas of the southeast United States
271 during the model period, from a range of ~ 1 to $2 \mu\text{g m}^{-3}$ to a range of ~ 1 to $4 \mu\text{g m}^{-3}$. While the
272 results of Pun (2008) for July 2, 2002 for this region using sesqui-MADRID indicate
273 significantly higher SOA levels, the corresponding percentage increases due to water uptake are
274 similar. The most affected region in Figure 1 is a ~ 500 km wide band from Louisiana through to
275 about Virginia. The mostly modest differences between the results from CMAQ-RH-2p and
276 UCD/CIT-RH-2p are consistent with the differences between the two models: 1) gas-phase
277 mechanisms used (SAPRC07, Carter (2010) vs. SPARC11, Carter (2013)); 2) meteorology
278 algorithm used (MM5 with nudging as described by Ngan et al. (2012) vs. WRFv.3.4 (WRF,
279 2014) with the NAM reanalysis data set); and 3) imposed limit (for model stability) on input RH
280 values assumed for water uptake (99% vs. 95%). Given the fact that RH values approaching
281 100% require amounts of condensed water that are large relative to any expected ambient OPM
282 levels, model instability at $\text{RH} \approx 100\%$ is to be expected in any model that considers co-
283 condensation of water. ζ_i values for organic compounds with the MCM-SOA model have been
284 found to be mostly in the range $0.33 < \zeta < 3$; the same was found to be true for the CMAQ-RH-
285 2p runs carried out here, except that for the SQT species values as large as 40 were often
286 calculated. For the CMAQ-RH-2p runs, $\zeta_{\text{water}} \approx 1$, due to the hydrophilicity of polar functional
287 groups on the SOA species.

288 Runs carried out using UCD/CIT-RH-2p allowing miscibility of the SOA and POA and
289 therefore water uptake into the total OPM did not significantly change the predicted levels of
290 SOA or associated water. In contrast to the results with CMAQ-RH-2p and UCD/CIT-RH-2p,
291 CMAQ-RH-MCM resulted in lower predicted increase in the levels of SOA because CMAQ-
292 RH-MCM forms mostly non-volatile SOA (which is not directly sensitive to RH effects). This is
293 consistent with the conclusions of others that MCM generally cannot explain observed ambient
294 OPM levels without arbitrary downward adjustment of the vapor pressures of semivolatile
295 products (Johnson et al, 2006), or by including other SOA generation pathways such as
296 formation of non-volatile products by reactive surface uptake (Li et al., 2015), as implemented
297 here in CMAQ-RH-MCM (see Figure 2).

298 The fourth column of panels in Figure 1 summarizes the findings for predicted water
299 uptake effects on SOA levels. For CMAQ-RH-2p and UCD/CIT-RH-2p, fractional increases as
300 large as 0.5 to 1.0 and higher (50 to 100% and higher) are indicated. Much weaker effects are
301 predicted for CMAQ-RH-MCM. The levels of water predicted to be present in the OPM for the
302 water uptake runs are given in Figure 1. In the Alabama/Georgia hotspot, CMAQ-RH-2p and
303 UCD/CIT-RH-2p give predicted organic aerosol water levels of ~ 0.5 to $2 \mu\text{g m}^{-3}$, nearly half
304 their predicted levels of SOA. The water levels predicted by CMAQ-RH-MCM are substantially
305 lower, and a consequence of the typically large estimated water activity coefficients in the
306 modeled OPM.

307 The CMAQ-RH-2p and UCD/CIT-RH-2p results may be more indicative of reality in this
308 region than those from CMAQ-RH-MCM, with the latter providing a lower limit estimation of
309 the SOA water effect. Consistent with our results are the indirectly measured particle water
310 levels reported by Guo et al. (2015) for the southeast United States. At four sites (three urban
311 and one rural) in Alabama and Georgia in 2012 (May through November), Guo et al. (2015)

312 report that OPM-associated water was “significant”, averaging 29 to 39% of all particle water.
313 Also, the OPM-associated water values were found to be correlated with the organic mass
314 fraction, and with RH.

315 Significant levels of water in OPM carry considerable importance for understanding the
316 levels and properties atmospheric OPM. First, the viscosity of many organic liquids decreases
317 strongly with increasing water content (*e.g.*, Acierno and Van Puyvelde, 2005), and decreasing
318 OPM viscosity facilitates gas/particle equilibration. Second, water content will affect the OPM
319 phase polarity, and liquid phase polarity affects reaction rates (much current discussion of OPM
320 formation processes involves condensed phase reactions). Third, the activity of water within an
321 OPM phase will obviously directly affect the rates of reactions that involve water, *e.g.*: a)
322 hemiacetal to acetal conversion (Jang and Kamens, 2001); b) organic ester and amide formation
323 Barsanti and Pankow, 2006); and c) sulfate ester formation (Surratt et al., 2007, 2008). Fourth,
324 particle water at levels as high as $10 \mu\text{g m}^{-3}$ in the southeast US and formed by condensation on
325 atmospheric sulfate has been proposed by Carlton and Turpin (2013) as an important compart-
326 ment for the uptake from the gas phase of water soluble organic compounds (*e.g.*, glyoxal (C_2),
327 methyl glyoxal (C_3), and higher carbon number compounds). However, uptake of such mole-
328 cules into water-rich OPM would compete non-negligibly with uptake into sulfate-associated
329 particle water, especially when electrolyte concentrations are high (Zuend and Seinfeld, 2012).

330 Overall, despite the model improvements discussed in this work, the predictive modeling
331 carried out here unquestionably still suffers greatly from many simplistic assumptions, *e.g.*, the
332 limited volatility range of the assumed 2p products, and the absence of a progression of second,
333 third, and higher generation products. Nevertheless, the results demonstrate that an MV
334 approach with water uptake is required when modeling OPM in the atmosphere.

335

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- 527

528 Figure Captions

529

530 Figure 1. 10-day averaged output in the surface layer from three molecular view-enabled
531 chemical transport models for August 29 through September 7, 2014 (after 1 to 5 days of
532 model spin-up). Surface layer = 0 to 34 m for PSU and TAMU, 0 to 50 m for UCD. For
533 CMAQ-RH-2p and UCD/CIT-RH-2p results, SOA and POA assumed immiscible; for
534 CMAQ-RH-MCM, SOA and POA assumed miscible. Base (B) case runs: **a.** Secondary
535 organic aerosol (SOA) levels with no water uptake. With water (W) uptake runs: **b.** SOA
536 levels as determined at each point (x,y,z,t) according to the local RH; **c.** Particle-phase water
537 levels within the OPM; and **d.** Fractional increases in predicted SOA levels as compared to
538 the base (B) case (no water uptake).

539

540 Figure 2. Stacked bar graphs for POA (primary organic aerosol), anthropogenic SOA (secondary
541 organic aerosol), biogenic SOA, and water (in OPM) for models run at PSU (CMAQ-RH-
542 2p), UCD (UCD/CIT-RH-2p), and TAMU (CMAQ-RH-MCM). Results are 10-day
543 averaged output in the surface layer for August 29 through September 7, 2014 (after 1 to 5
544 days of model spin-up). Surface layer = 0 to 34 m for PSU and TAMU, 0 to 50 m for UCD;
545 SOA and POA assumed immiscible. The base (B) case runs assumed no water uptake. For
546 the PSU and UCD runs, the with water (W) uptake runs assumed water co-condensation into
547 the SOA only as determined at each point (x,y,z,t) according to the local RH. For the TAMU
548 runs, the W runs assumed water co-condensation into the mixed SOA+POA at each point
549 (x,y,z,t) according to the local RH.

550

Table 1. Details for Three Applications of Chemical Transport Models in a Molecular View (MV) of Secondary Organic Aerosol (SOA) Formation with Water Uptake.

ACCEPTED MANUSCRIPT				
<i>Common features across the applications:</i>				
<p>a) emissions: anthropogenic inputs generated from the 2005 National Emission Inventory (NEI); biogenic inputs generated using the Biogenic Emissions Inventory, Version 3 (BEIS3); all inputs processed using the Sparse Matrix Operator Kernel Emission (SMOKE) model;</p> <p>b) condensed compounds: SOA compounds are formed by initial reaction of volatile organic compounds (VOCs); some of the SOA material is assumed to become non-volatile, as assumed in CMAQ 4.7.1; POA inputs are considered non-volatile for all model time, as assumed in CMAQ 4.7.1;</p> <p>c) water: $RH > 0$ causes water uptake into OPM;</p> <p>d) activity coefficients: composition-dependent ζ_i values in the absorbing phase are calculated using UNIFAC.</p>				
Application (SOA framework, and gas phase chemical mechanism)	<u>Molecular view (MV) of Condensed SOA and POA</u>			
	SOA semi-volatile portion	SOA non-volatile portion	POA	Characteristics of <u>OPM Phase(s)</u>
<p><i>CMAQ-RH-2p</i>^a (CMAQ 4.7.1^b, with AERO5 and SAPRC07)</p>	<p>1. Structural features (carbon number n_C and numbers of functional groups) assigned to the 12 hypothetical, 2p type products in CMAQ 4.7.1 for oxidation of seven hydrocarbon SOA precursors;</p> <p>2. The structural features of each product chosen so that the predicted K_p value matched the K_p value used in CMAQ 4.7.1 for 298 K (see Table 2);</p> <p>3. Dependence of K_p on T computed as in CMAQ 4.7.1.</p>	<p>1. Structural features (carbon numbers and numbers of functional groups) assigned to six of the hypothetical non-volatile lumped products assumed by CMAQ 4.7.1 to form via oxidation pathways starting in the gas-phase: three products for the direct oxidation of aromatic SOA precursors via the low-NO_x pathway; one accretion (aka “oligomer”) product from aging^c of condensed anthropogenic SOA products; one accretion product from aging of biogenic SOA products; one product from the acid-catalyzed reaction of isoprene;</p> <p>2. Assigned structural features consistent with negligible volatility under ambient conditions as well as structures reported for chamber organic particulate matter;</p> <p>3. Cloud processing of glyoxal/methylglyoxal excluded.</p>	<p>Retained anonymized as in CMAQ 4.7.1 because POA was assumed non-miscible with SOA (POA structures are then not needed for MV modeling of SOA).</p>	<p>1. Absorbing phase = non-vol. SOA + semi-vol. SOA + water; and</p> <p>2. POA considered a separate phase because that is most consistent with low-polarity POA. (Unmodified CMAQ 4.7.1 simply assumes POA and SOA are miscible.)</p>
<p><i>UCD/CIT-RH-2p</i>^d (CMAQ 4.7.1 as deployed in UCD/CIT^e, with SAPRC11)</p>	<p>Same as above.</p>	<p>Same as above.</p>	<p style="text-align: center;"><i>option 1</i></p> <p>POA retained anonymized as above</p> <p style="text-align: center;"><i>option 2</i></p> <p>POA assigned a mix of four specific structures (C₂₅ alkanes, levoglucosan, monoglyceride, and C₁₈ acid)</p>	<p>1. Absorbing phase = non-vol. SOA + semi-vol. SOA + water; and</p> <p>2. POA non-miscible and non-sorbing.</p> <p>Absorbing phase = all OPM + water. (POA miscible and sorbing.)</p>
<p><i>CMAQ-RH-MCM</i>^f (CMAQ 4.7.1 as deployed in MCM-SOA^g, with MCM)</p>	<p>1. The Master Chemical Mechanism (MCM) was used to generate specific condensable organic products of atmospheric oxidation as in Li et al. (2015)</p> <p>2. Dependence of K_p on T computed as in Li et al. (2015)</p>	<p>1. Specific accretion products (aka “oligomers”) were considered to form by aging³ of the condensed-phase portions of the MCM-generated products;</p> <p>2. Specific chemical structures were assumed for the non-volatile products of acid-catalyzed reaction of isoprene;</p> <p>3. Specific non-volatile products were assumed for the reactive surface uptake of 1,4-dicarbonyl compounds and isoprene epoxydiol.</p>	<p>POA represented using a mixture of eight specific structures and assumed miscible.</p>	<p>Absorbing phase = all OPM + water.</p>

^aRuns were carried out on the “CsAR” computer cluster at PSU;

^bCommunity Multi-Scale Air Quality Model, version 4.7.1, see Carlton et al. (2010);

^cAll semi-volatile products converted to non-volatile products with rate constant $k_{\text{orig}} = 9.6 \times 10^{-6} \text{ s}^{-1}$;

^dRuns were carried out on the “Wolf” computer cluster at University of California at Davis;

^eKleeman and Cass (2001); Ying et al. (2008);

^fRuns were carried out on the “eos” computer cluster at the Texas A&M University, and the on the “lonestar” computing cluster in the Texas Advanced Computing Center at University of Texas as Austin.

^gLi et al. (2015).

Table 2.a. Semi-volatile CMAQ 2p Products for Secondary Organic Aerosol (SOA) Formation with Assigned Molecular View (MV) Characteristics as Used in CMAQ-RH-2p and UCD/CIT-RH-2p.

Characteristics in CMAQ 4.7.1		vapor pressure from B (using G)	Assigned Molecular View (MV) Characteristics (D through H) (Consistent with Inferred p_L° , as based on Pankow and Asher (2008))										
A	B	C	D	E							F	G	H
2p product	$1/C^* = K_p$ (298 K)	inferred p_L° (atm) (298 K)	assumed number of carbons n_C	numbers of UNIFAC groups assigned to structure to match (with n_C) the inferred p_L° (UNIFAC group number)							formula	MW (g/mol)	OM/OC
				E1 CH3 (1)	E2 CH2 (2)	E3 CH (3)	E4 OH (15)	E5 CH2CO (20)	E6 CHO (21)	E7 COOH (43)			
ALK	50.0	2.72E-12	7	2	2	2	3	0	0	1	C ₇ H ₁₆ O ₅	180	2.14
BNZ1	3.3	4.58E-11	5	0	0	0	0	1	1	2	C ₆ H ₅ O ₆	161	2.68
BNZ2	9.0E-03	2.03E-08	5	1	1	1	2	0	2	0	C ₆ H ₁₂ O ₄	134	2.23
ISO1	8.6E-03	2.15E-08	5	0	0	3	3	1	0	0	C ₅ H ₈ O ₄	132	2.20
ISO2	1.6	1.13E-10	5	0	0	5	4	0	0	0	C ₅ H ₉ O ₄	133	2.23
SQT	0.08	1.09E-09	15	5	4	0	0	2	2	0	C ₁₅ H ₂₄ O ₄	273	1.52
TOL1	0.43	3.49E-10	6	1	1	1	2	1	0	1	C ₆ H ₁₁ O ₅	163	2.26
TOL2	4.7E-02	2.97E-09	8	2	2	2	1	0	1	1	C ₈ H ₁₅ O ₄	175	1.82
TRP1	0.13	1.03E-09	8	2	2	2	3	1	0	0	C ₈ H ₁₇ O ₄	177	1.84
TRP2	9.0E-03	1.37E-08	9	0	1	1	0	2	3	0	C ₉ H ₁₀ O ₅	198	1.83
XYL1	0.76	1.85E-10	6	0	0	0	0	2	0	2	C ₆ H ₆ O ₆	174	2.42
XYL2	2.9E-02	4.55E-09	8	0	1	1	0	2	1	1	C ₈ H ₉ O ₅	185	1.93

Table 2.b. Non-Volatile CMAQ Products from Condensed 2p Secondary Organic Aerosol (SOA) Products with Assigned Molecular View (MV) Characteristics as Used in CMAQ-RH-2p and UCD/CIT-RH-2p.

Characteristics in CMAQ 4.7.1		vapor pressure from B (using G)	Assigned Molecular View (MV) Characteristics (D through H) (Consistent with Inferred p_L° , as based on Pankow and Asher (2008))										
A	B	C	D	E							F	G	H
non-volatile product	$1/C^* = K_p^a$ (298 K)	inferred p_L° (atm) (298 K)	assumed number of carbons n_C	numbers of UNIFAC groups assigned to structure to match (with n_C) the inferred p_L° (UNIFAC group number)							formula	MW ^b (g/mol)	OM/OC
				E1	E2	E3	E4	E5	E6	E7			
				CH3 (1)	CH2 (2)	CH (3)	OH (15)	CH2CO (20)	CHO (21)	COOH (43)			
BNZ3 ^c	9.7E03	1.43E-14	5	0	0	3	3	0	0	2	C ₅ H ₁₁ O ₇	180	3.0
TOL3 ^d	2.3E04	5.39E-15	6	0	1	3	3	0	0	2	C ₆ H ₁₀ O ₇	194	2.7
XYL3 ^e	2.0E04	1.18E-13	8	0	1	4	1	0	0	3	C ₈ H ₁₀ O ₇	218	2.3
ISO3 ^f	5.0E04	2.32E-15	8	2	1	5	6	0	0	0	C ₈ H ₁₉ O ₆	211	2.2
OLGA ^g	8.3E03	1.43E-14	7	0	2	2	1	0	0	3	C ₇ H ₁₀ O ₇	206	2.5
OLGB ^h	1.3E05	7.58E-16	10	1	3	3	1	0	0	3	C ₁₀ H ₁₆ O ₇	248	2.1

^aAt all realistic values of SOA mass concentration, these large K_p values give $f_p \approx 1$ (compound is essentially non-volatile, see Eq.(4)). These assignments are consistent with the practice in CMAQ4.7.1 of simply assigning all non-volatile SOA compounds to the particle phase, and not calculating f_p .

^bPrecedence for assigning MW was given to roughly matching the values given in CMAQ4.7.1, even though ostensibly some of the presumed non-volatile products are accretion products of some type. Little change in the simulation output would have resulted from assigning higher MW values while preserving carbon mass in the semi-volatile \rightarrow non-volatile conversion step.

^cBased roughly on a structure discussed by Sato et al. (2012).

^dBased roughly on a structure discussed by Baltaretu et al. (2009).

^eRoughly a dimer of a structure discussed by Smith et al. (1999).

^fSimilar to a structure discussed by Surratt et al. (2006).

^g Roughly a dimer of a structure discussed by Calvert et al. (2002).

^hBased on Scheme 7 of Warscheid and Hoffmann (2001).

figure 1 with all individual elements, better quality overall

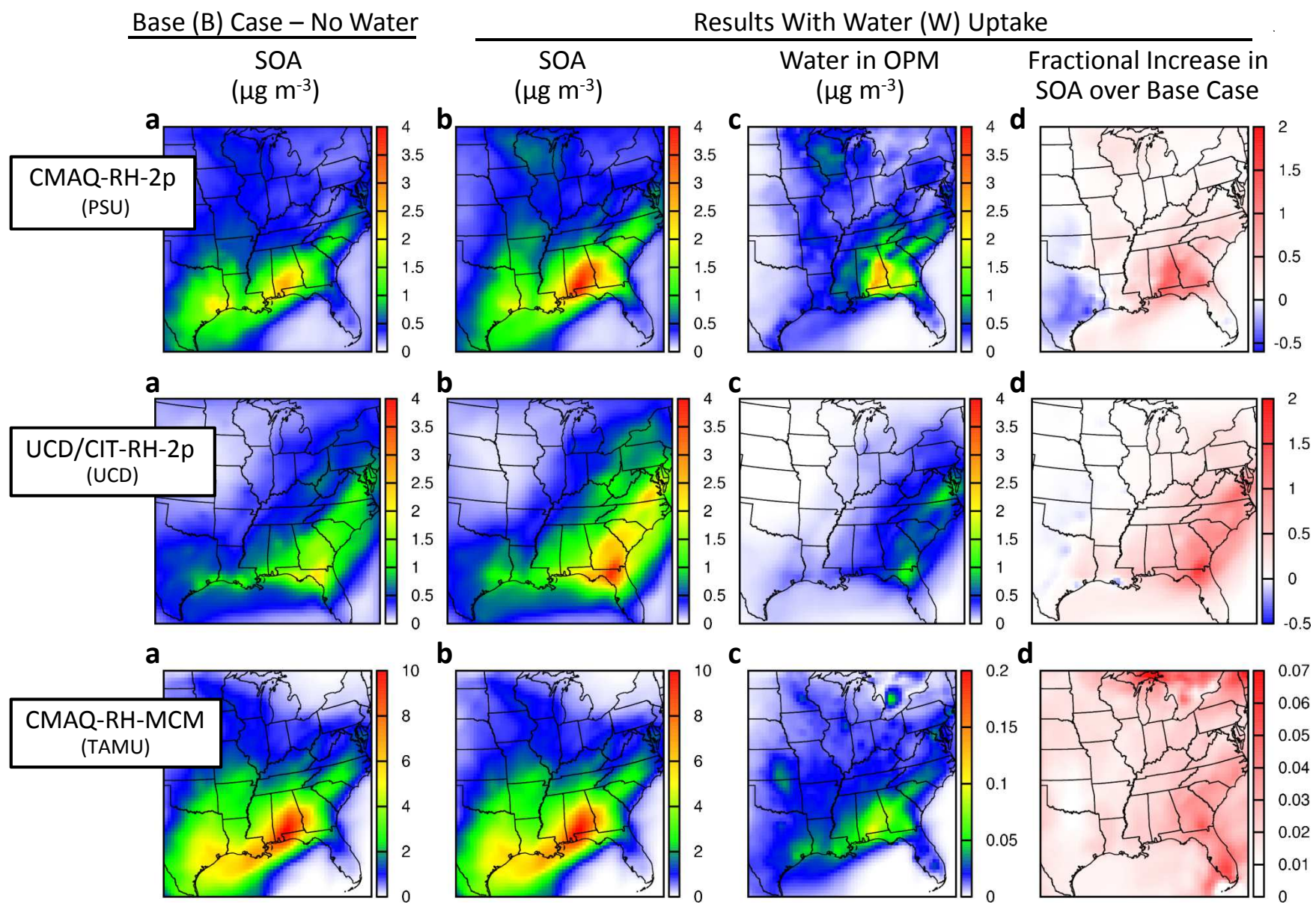


figure 1 as single image

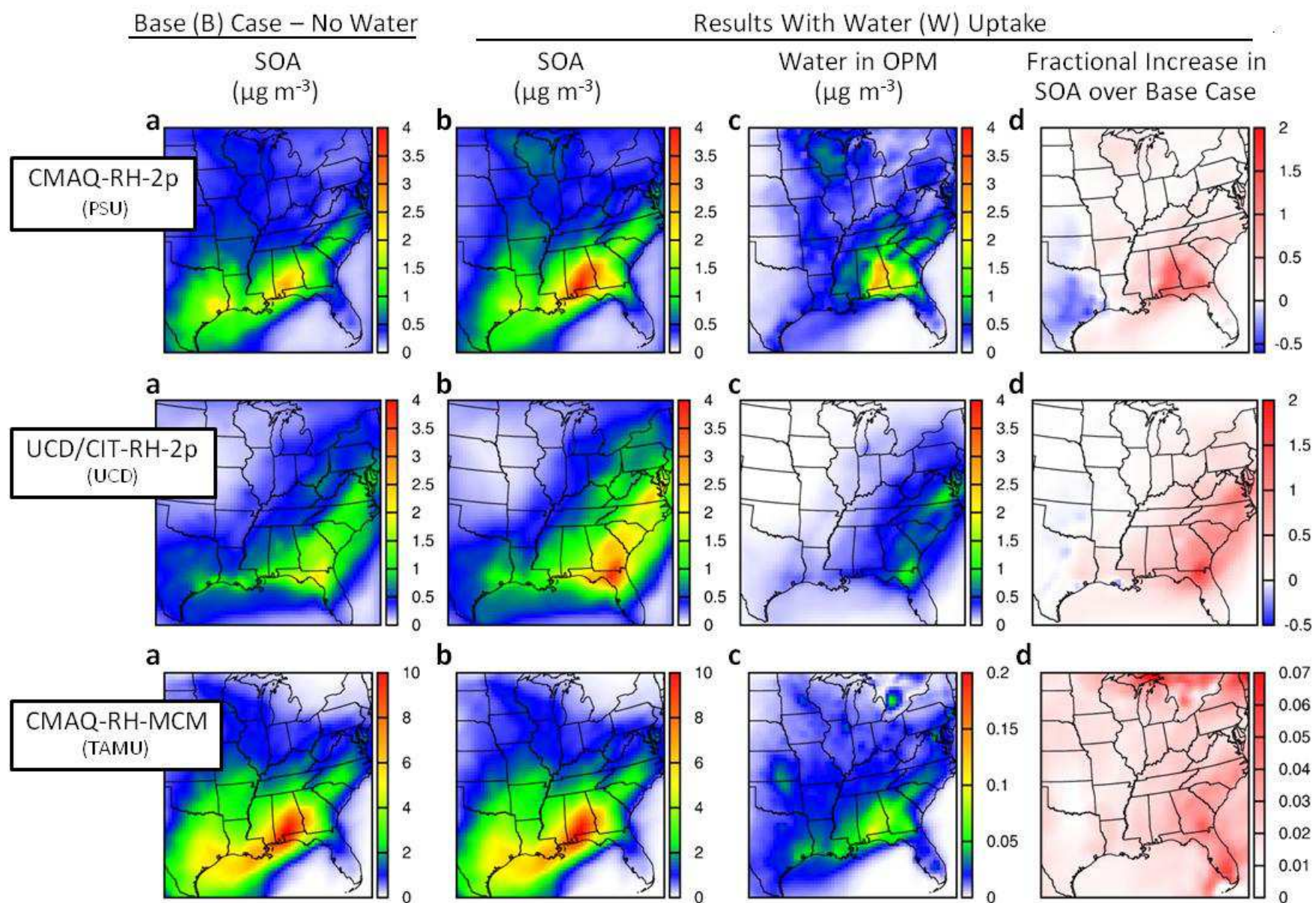


figure 2 with all individual elements, better quality overall

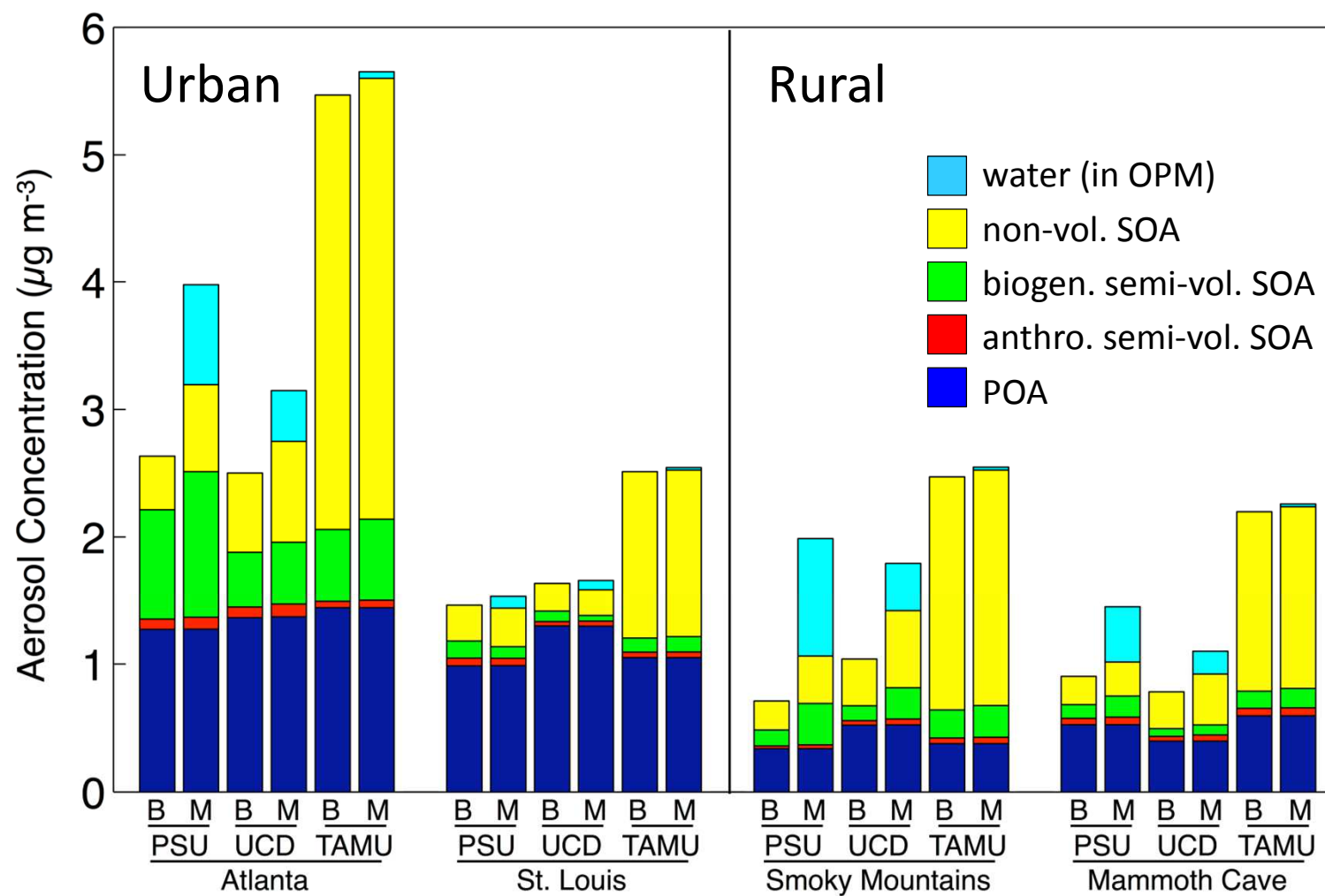
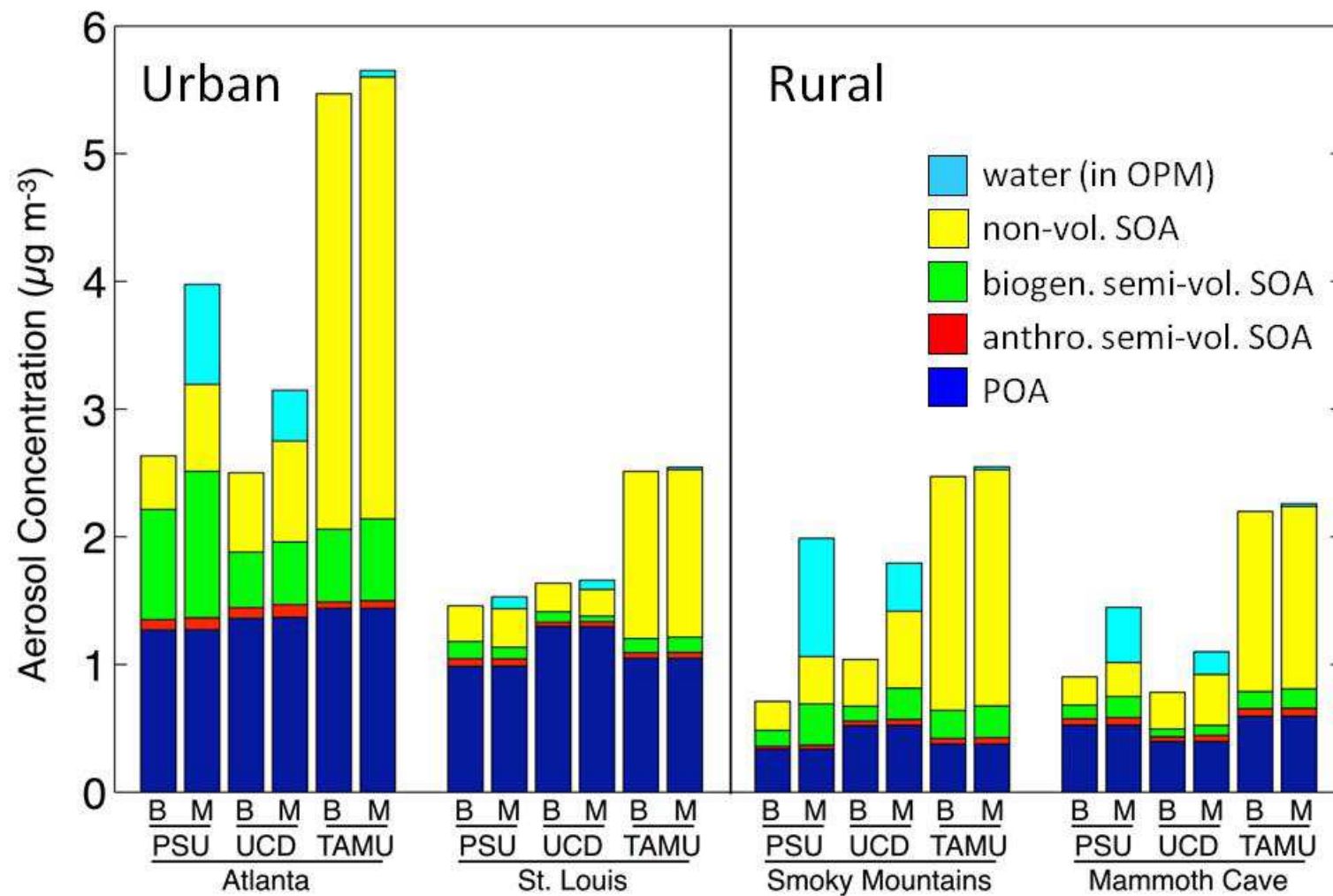


figure 2 as single image



HIGHLIGHTS

- Current 3-D transport models use anonymized view modeling of organic particulate matter (OPM).
- Anonymized view modeling assigns only a volatility (vapor pressure) to each OPM constituent.
- Anonymized view modeling cannot consider effects of water uptake on OPM levels.
- Molecular view modeling assigns structural features to each OPM constituent.
- Molecular view modeling can consider effects of water uptake on OPM levels and OPM properties.