

1 Modeling Regional Air Quality and Climate: Improving Organic Aerosol and Aerosol Activation
2 Processes in WRF/Chem version 3.7.1
3

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17 **ABSTRACT**

18 Air quality and climate influence each other through the uncertain processes of aerosol formation
19 and cloud droplet activation. In this study, both processes are improved in the Weather, Research
20 and Forecasting model with Chemistry (WRF/Chem) version 3.7.1. The existing Volatility Basis
21 Set (VBS) treatments for organic aerosol (OA) formation in WRF/Chem is improved by
22 considering the secondary OA (SOA) formation from semi-volatile primary organic aerosol
23 (POA), a semi-empirical formulation for the enthalpy of vaporization of SOA, as well as
24 functionalization and fragmentation reactions for multiple generations of products from the
25 oxidation of VOCs. Two-month long simulations (May to June 2010) are conducted over
26 continental U.S. and results are evaluated against surface and aircraft observations during the
27 Nexus of Air Quality and Climate Change (CalNex) campaign. Among all the configurations
28 considered, the best performance is found for the simulation with the 2005 Carbon Bond
29 mechanism (CB05) and the VBS SOA module with semivolatile POA treatment, 25%

30 fragmentation, and the emissions of semi-volatile and intermediate volatile organic compounds
31 being 3 times of the original POA emissions. Among the three gas-phase mechanisms (CB05,
32 CB6, and SAPRC07) used, CB05 gives the best performance for surface ozone and PM_{2.5}
33 concentrations. Differences in SOA predictions are larger for the simulations with different VBS
34 treatments (e.g., non-volatile POA ~~vs.~~versus semivolatile POA) as compared to the simulations
35 with different gas-phase mechanisms. Compared to the simulation with CB05 and the default SOA
36 module, the simulations with the VBS treatment improve cloud droplet number concentration
37 (CDNC) predictions (NMBs from -40.8% to a range of -34.6% to -27.7%), with large differences
38 between CB05/CB6 and SAPRC07 due to large differences in their OH and HO₂ predictions. An
39 advanced aerosol activation parameterization based on the FN05 series reduces the large negative
40 CDNC bias associated with the default ARG00 parameterization from -35.4% to a range of -0.8%
41 to 7.1%_; lit, however, increases the errors due to overpredictions of CDNC, mainly over
42 northeastern U.S. This work indicates a need to improve other aerosol-cloud-radiation processes
43 in the model such as the spatial distribution of aerosol optical depth and cloud condensation nuclei
44 in order to further improve CDNC predictions.

45 **1. Introduction**

46
47 The Intergovernmental Panel on Climate Change (IPCC) report on the AR5 scenario attributes
48 the aerosol radiative forcing (RF) to be the dominant source of uncertainty contributing to the
49 overall uncertainty in the net Industrial Era Radiative Forcing (RF) calculations (Myhre et al.,
50 2013). Despite the inclusion of more aerosol processes in the current generation of atmospheric
51 models, differences between atmospheric models and observations continue to persist. Aerosols
52 affect the climate through the direct effect by absorbing or scattering radiation, or the indirect
53 effect by acting as cloud condensation nuclei (CCN). According to Hallquist et al. (2009), the

54 formation of inorganic particulates such as sulfate, nitrate, and ammonium are well understood,
55 however, there are large uncertainties in the formation of secondary organic aerosol (SOA). As a
56 result, current models do not have a comprehensive treatment of OA, which usually result in an
57 underprediction of OA concentrations (Hodzic et al., 2010; Jathar et al., 2011; Bergstrom et al.,
58 2012), due to missing key precursors and processes in OA formation (Ahmadov et al., 2012). Some
59 of the missing key precursors in most models include semi-volatile primary organic aerosol (POA),
60 long-chain *n*-alkanes, polycyclic aromatic hydrocarbons (PAHs), and large olefins that have lower
61 volatilities compared to traditional SOA precursors (Chan et al., 2009). The organic carbon (OC)
62 component of the radiative forcing in the IPCC AR5 report also does not include SOA with the
63 reason that the formation is dependent on a number of factors that are not currently sufficiently
64 quantified (Myhre et al., 2013). However, SOA can form a significant percentage of total OA (up
65 to 95% in rural areas) (Zhang et al., 2007). Another large source of uncertainty is the quantification
66 of clouds as well as aerosol-cloud interactions due to incomplete or inaccurate representations of
67 these processes in climate models (Boucher et al., 2013). A major process in cloud formation from
68 aerosol is aerosol activation, which involves the condensational growth of aerosols in a cooling air
69 parcel until maximum supersaturation, and some of the wet particles reach a critical radius where
70 they are then able to grow spontaneously into cloud droplets (Ghan et al., 2011). Various
71 approaches have been developed to reduce the uncertainties associated with OA and aerosol
72 activation treatments in climate models. Those treatments are reviewed in the following section.

73 **1.1. VBS Treatments and Sensitivity to Different Gas-Phase Chemical Mechanisms in** 74 **Regional and Global Models**

75
76 Unlike inorganic aerosols such as sulfate, the physical and chemical properties of OA
77 dynamically evolve with age (Jimenez et al., 2009). The traditional approach to modeling SOA is

78 to assume that each VOC precursor forms several surrogate compounds (Odum et al., 1996).
79 However, the traditional method has several shortcomings, for example, two products are needed
80 for each VOC precursor causing this method to be computationally-expensive if many VOC
81 precursors are treated in the model (Murphy and Pandis, 2009). The assumption that the products
82 are unreactive also does not reflect the dynamic nature of the first generation products from the
83 oxidation of VOCs that can undergo successive oxidation steps to further produce lower volatility
84 products (Jimenez et al., 2009). The volatility basis set (VBS) is a framework developed by
85 Donahue et al. (2006), which is able to simulate gas-phase partitioning and multiple generations
86 of gas-phase oxidation of organic vapors. This approach addresses the shortcomings of the
87 traditional SOA modeling approach as it can cover the complete volatility range of OA compounds
88 (Murphy and Pandis, 2009).

89 Table 1 summarizes some of the VBS treatments from current regional and global models. The
90 VBS treatment has been implemented into a number of regional models such as the Weather,
91 Research and Forecasting model with Chemistry (WRF/Chem) (Shrivastava et al., 2011;
92 Ahmadov et al., 2012), the Particulate Matter Comprehensive Air Quality Model with extensions
93 (PMCAMx) (Lane et al., 2008; Donahue et al., 2009; Murphy et al., 2009), and CHIMERE (Hodzic
94 et al., 2010). It has also been implemented in global models such as GISS II' GCM (Farina et al.,
95 2010; Jathar et al., 2011) and the Community Earth System Model (CESM) (Shrivastava et al.,
96 2015). Different studies define the classifications of the organic species slightly differently.
97 Donahue et al. (2009) defined primary organic vapors with effective saturation concentrations (C^*)
98 of 10^{-2} - 10^{-1} , 10^0 - 10^2 , and 10^3 - 10^6 $\mu\text{g m}^{-3}$ at 298 K to be low volatility organic compounds
99 (LVOCs), semi-volatile organic compounds (SVOCs), and intermediate volatility organic
100 compounds (IVOCs), respectively. Shrivastava et al., (2011) and Jathar et al. (2011) defined

101 primary organic vapors with C^* values of 10^{-2} - 10^3 and 10^4 – 10^6 $\mu\text{g m}^{-3}$ to be SVOCs and IVOCs,
102 respectively. All those studies defined VOCs to be gas-phase organic species with C^* larger than
103 10^6 $\mu\text{g m}^{-3}$ at 298 K.

104 The traditional emission inventories used in the chemical transport models consist of VOCs
105 but not SVOCs or IVOCs as both SVOCs and IVOCs are difficult to measure. This is most likely
106 because SVOCs and IVOCs tend to evaporate at high temperatures from combustion sources
107 (Donahue et al., 2009). As the traditional SOA approach usually underpredicts the SOA
108 concentration, the addition of the SVOC and IVOC emissions on top of the existing VOC
109 emissions in most emission inventories can improve model performance. To account for the
110 missing key precursors in OA formation, SVOC and IVOC emissions are usually estimated as a
111 factor of existing POA emissions in current emission inventories. For example, Shrivastava et al.
112 (2011) estimated the sum of all SVOC and IVOC precursors to be 7.5 times the mass of traditional
113 POA emissions inventory over Mexico City, but indicated that the scaling factor of 3 for SVOC
114 emissions based on the POA emissions is poorly constrained. Shrivastava et al. (2008) and Jathar
115 et al. (2011) assumed that SVOC emissions are represented by the traditional emission inventory
116 while IVOC emissions are 1.5 times the traditional emission inventory. Pye and Seinfeld (2010)
117 assumed that SVOC emissions are a subset of traditional POA emission inventories, and their POA
118 emissions were scaled up by 27% on a global scale. IVOC emissions are assumed to be spatially-
119 distributed similar to naphthalene and are predicted to be roughly a factor of half of global POA
120 emissions. Tsimpidi et al. (2014) assumed that the IVOC emissions are 1.5 times the traditional
121 POA emission inventory and are assigned to the 4th volatility bin with $C^* = 10^5$ $\mu\text{g m}^{-3}$. For
122 comparison, some studies such as Ahmadov et al. (2012) and Bergstrom et al. (2012) used the
123 VBS approach for OA modeling but did not include additional SVOC emissions. There are also

124 differences in the volatility distribution used in literature. Shrivastava et al. (2008) and Jathar et
125 al. (2011) found that moving half the mass of SVOC from all bins to the lowest bin from the
126 traditional “diesel exhaust” volatility distribution of Robinson et al. (2007) produced the lowest
127 errors in simulated OA on an annual average basis.

128 The number of bins used can also result in differences in simulated SOA concentrations.
129 Shrivastava et al. (2011) showed that the 2-species VBS performed better than the 9-species VBS
130 in modeling oxygenated organic aerosol (OOA) and gave the closest agreement to the OOA
131 calculated by the Positive Matrix Factorization (PMF) method. This indicates that SOA may be
132 less volatile as compared to the volatility distribution in the 9-species VBS which allows for
133 evaporation of SOA with dilution (Shrivastava et al., 2011).

134 The amount of oxygen added for each oxidation step may contain uncertainties. This factor
135 can influence the O:C ratio used for the model evaluation. O:C predictions from models need to
136 be improved by including fragmentation reactions (which could lead to an increase in O:C ratios)
137 and improving emission estimates (Shrivastava et al., 2011). Different rate constants can also result
138 in different predictions of SOA concentrations. For example, Farina et al. (2010) showed that the
139 use of k value of $1 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ compared to the default k value of $10 \times 10^{-12} \text{ cm}^3$
140 $\text{molecule}^{-1} \text{ s}^{-1}$ resulted in a reduced aged SOA formation by 71%. Hodzic et al. (2010) also showed
141 a case study based on Grieshop et al. (2009) in which each oxidation step reduced the volatility of
142 the S/IVOC vapors by two orders of magnitude and each successive oxidation step produced a
143 40% increase in mass due to the addition of oxygen. This case is inconclusive in urban areas - a
144 larger bias along with a higher correlation coefficient compared to the more common case where
145 each oxidation step reduced the volatility by one order of magnitude with a 7.5% increase in mass.

146 However, the model performed worse (with larger bias and lower correlation coefficient) in
147 suburban areas.

148 The aging process improves model performance in general in the United States (U.S.) but
149 deteriorates the performance in several parts of Europe. Accounting for the aging process of OA
150 will increase the OA concentrations and improve model results in the U.S. where OA is usually
151 underpredicted, but increase the model bias for OA in several parts of Europe where OA
152 concentrations are overpredicted (Farina et al., 2010; Bergstrom et al., 2012).

153 Shrivastava et al. (2013) studied the effects of the fragmentation and functionalization in VBS.
154 Functionalization increases the mass of OA for each successive oxidation step, while
155 fragmentation reduces the mass for each oxidation step. One such a case includes simulating first-
156 order effects of the fragmentation and functionalization processes in VBS by assuming
157 functionalization of 100% of organic vapors for the first two generations of oxidation and both
158 fragmentation and functionalization for the third and higher generations of oxidation. The
159 fragmentation reduces the SOA concentrations drastically. For example, Shrivastava et al. (2013)
160 showed that peak SOA concentrations can be reduced by factors of 2 to 4 for a 1-hour example on
161 10 March 2006 at 21 UTC over Mexico City Plateau.

162 The VBS framework for OA modeling in the latest version of WRF/Chem, v3.7.1, is coupled
163 with several gas-phase mechanisms including the 2005 Carbon Bond Mechanism (CB05)
164 (Yarwood et al., 2005), the Model for Ozone and Related chemical Tracers version 4 (MOZART-
165 4) (Emmons et al., 2010), the Regional Atmospheric Chemistry Model (RACM) (Stockwell et al.,
166 1997), and the 1999 version of the Statewide Air Pollution Research Centre (SAPRC99)
167 mechanism (Carter, 2000). Different gas-phase mechanisms have different lumpings/groupings
168 for VOCs, which will affect OA formation. For example, VOCs are lumped according to their

169 carbon bonds (e.g., single or double bond) in CB05 (Yarwood et al., 2005) while VOCs in
170 SAPRC99 (Carter, 2000) are lumped according to their OH reactivities. A number of studies
171 examined the differences in predicting O₃ concentrations due to different gas-phase mechanisms
172 (e.g., Luecken et al., 2008; Li et al., 2012; Shearer et al., 2012; Zhang et al., 2012), but fewer
173 studies reported the impact of different gas-phase mechanisms on modeling SOA and PM_{2.5}
174 concentrations (Kim et al., 2011; Zhang et al., 2012). SAPRC99 has more detailed organic
175 chemistry compared to CB05. SAPRC99 has been updated to SAPRC07 (and recently, to
176 SAPRC11) based on newly available information regarding the reactions and influence of
177 individual VOCs on O₃, as well as evaluations against chamber experiments (Carter, 2010). In
178 addition, SAPRC07 has reformulated reactions of peroxy radicals so that the effects of changes in
179 nitrogen oxides (NO_x) on organic product formation is more accurately represented. SAPRC07
180 has the most extensive set of VOC species and reactions, as compared to CB05 and the Carbon
181 Bond version 6 (CB6). Shearer et al. (2012) reported that a condensed version of SAPRC07
182 predicted lower O₃ and OH concentrations in central California compared to SAPRC99 due to a
183 decreased reaction rate coefficient in the reaction of OH and NO₂ to form HNO₃. Li et al. (2012)
184 also showed that predicted O₃ concentrations from SAPRC07 were lower than those of SAPRC99
185 by up to 20% over Texas. The same study also reported that SAPRC07 gave lower OH
186 concentrations due to differences in the reaction rate constants in the reactions of O¹D and H₂O
187 between SAPRC07 and SAPRC99. Luecken et al. (2008) reported that SAPRC99 gave higher O₃
188 concentrations compared to CB05 on average; however, the differences vary with locations,
189 VOC/NO_x ratios, and the concentrations of precursor pollutants. This is consistent with the results
190 from Zhang et al. (2012), which predicted that SAPRC99 using WRF/Chem with the Model of
191 Aerosol, Dynamics, Reaction, Ionization and Dissolution (WRF/Chem-MADRID) produced the

192 highest O₃ mixing ratios in July at the Southeastern Aerosol Research and Characterization
193 (SEARCH) sites. The CB6 (Yarwood et al., 2010) is an updated version of CB05 with improved
194 kinetic and photolysis data, additional explicit species for long-lived and abundant organic
195 compounds including propane, acetone, benzene and acetylene, as well as revised isoprene and
196 aromatics chemistry from CB05. Yarwood et al. (2010) showed that CB6 produces higher daily
197 maximum 8-hr O₃ as compared to CB05 over Los Angeles for one episode day in August with the
198 highest observed O₃ mixing ratios. CB6 was also shown to produce substantially higher OH
199 concentrations (25% to 50% higher at mid-day over large areas) over eastern U.S. compared to
200 CB05 over a few days in June, 2006. A summary of the main characteristics of CB05, CB6, and
201 SAPRC07 gas-phase mechanisms are listed in Table 2.

202 **1.2. Description of Aerosol Activation Parameterizations**

203
204 Ghan et al. (2011) provided a comprehensive review on various aerosol activation treatments
205 in current climate models. Two main types of parameterizations are commonly used: the Abdul-
206 Razzak and Ghan (2000) (AR-G00) and the Fountoukis and Nenes (2005) (FN05) and associated
207 updates described in Barahona et al. (2010) and Morales Betancourt and Nenes (2014). AR-G00
208 uses multiple lognormal or sectional distributions to approximate the aerosol size distribution. It
209 uses the Kohler theory to relate the aerosol size distribution and composition to the number of
210 aerosols activated as a function of maximum supersaturation (S_{\max}). The complex function
211 involving S_{\max} is parameterized based on the standard deviation σ from a large number of
212 numerical solutions using a cloud parcel model. The number and mass activated are particles with
213 critical supersaturation less than S_{\max} . It also accounts for particle growth before and after the
214 particles are activated. However, the ARG treatment does not explicitly represent kinetic
215 limitations which tend to affect smaller or larger particles (with diameters far from their critical

216 size). Very small particles tend to lose water when supersaturation declines as they never exceed
217 the critical supersaturation for that particle size, and very large particles may not have achieved
218 the critical size before S_{\max} is reached (Ghan et al., 2011). Kinetic limitations refer to the (i) inertial
219 mechanism – where particles with large dry diameters grow to be as large as activated particles
220 but have not been activated themselves, these particles should be considered together with
221 activated particles; (ii) evaporation mechanism – where particles with high critical supersaturation
222 evaporate before reaching their critical diameters; and the (iii) deactivation mechanism – where
223 initially activated particles that are deactivated to interstitial aerosols when the parcel
224 supersaturation falls below the equilibrium supersaturation (Nenes et al., 2001). Neglecting kinetic
225 limitations performs well for all conditions except in highly-polluted areas (Ghan et al., 2011). In
226 urban and highly-polluted cases, many particles fail to be activated due to strong evaporation and
227 deactivation processes (Nenes et al., 2001). Explicitly accounting for kinetic limitations reduces
228 CDNC at low updraft velocity (Ghan et al., 2011).

229 The Fountoukis and Nenes (2005) (FN05) scheme improved the ARG00 scheme by solving
230 S_{\max} analytically (with the exception of kinetically-limited particles) using a so-called “population
231 splitting” method. In addition, FN05 took into account the kinetic limitations, as well as the
232 influence of gas kinetics on water vapor diffusivity (Ghan et al., 2011). The other improved
233 treatments built on top of the FN05 scheme include the entrainment of ambient air, which could
234 reduce the supersaturation of the updraft (Barahona and Nenes, 2007) (BN07) (therefore reducing
235 CDNC); the adsorption of water vapor onto insoluble particles by Kumar et al. (2009) (KU09)
236 based on a modified Frenkel-Halsey-Hill (FHH) adsorption theorem (which will increase CDNC);
237 the growth of giant cloud condensation nuclei (CCN) (Barahona et al., 2010) (BA10) by
238 introducing an additional condensation rate term to account for condensation of giant CCN (which

239 will reduce CDNC); as well as the modification of the original population splitting concept in
240 FN05 and BA10 by Morales Betancourt and Nenes (2014) (MN14) by better accounting for the
241 size of inertially limited CCN, and removing a discontinuity in the calculation of the surface area
242 of cloud droplets.

243 The parameterization of Abdul Razzak and Ghan (2000) (ARG00) is used as the default
244 aerosol activation module in WRF/Chem. It is not linked to the microphysics module or cumulus
245 parameterization in WRF or WRF/Chem. However, for WRF/Chem, the cloud droplet number
246 concentration (CDNC) generated in ARG00 is passed to the microphysics scheme, i.e., the
247 Morrison two-moment microphysics scheme selected in this work.

248 **1.3 Motivations and Objectives**

249
250 The online-coupled meteorology and chemistry model, WRF/Chem, has recently been
251 applied for air quality and climate modeling on a decadal scale (Yahya et al., 2016a, b).
252 WRF/Chem can also simulate aerosol direct and indirect feedbacks, which are important
253 considerations for climate modeling. However, as mentioned previously, the representations of
254 OA and aerosol-cloud interactions in current regional and global climate models are subject to
255 large uncertainties. In particular, while the VBS framework in WRF/Chem significantly improves
256 SOA performance (Wang et al., 2015), it lacks the semi-volatile POA treatment, as well as
257 fragmentation processes (Shrivastava et al., 2013). The first objective of this study is to reduce
258 uncertainties associated with OA predictions by improving the existing VBS module in
259 WRF/Chem and identifying the best gas-phase chemical mechanism to drive the VBS module for
260 the most accurate OA predictions. The impact of the improved OA predictions on CDNC in
261 WRF/Chem will be quantified. The second objective is to incorporate an improved aerosol

262 activation parameterization based on the FN05 series into WRF/Chem to study its impacts on
263 CDNC predictions.

264 **2. Model Configuration, Evaluation Protocol, and Observational Datasets**

265

266 **2.1. Model Setup and Inputs**

267

268 The model used in this study is a modified version of WRF/Chem v3.7.1 as described by Wang
269 et al. (2015). The 2005 Carbon Bond gas-phase mechanism (CB05) of Yarwood et al. (2005) with
270 additional chlorine chemistry is coupled with the Modal for Aerosol Dynamics in Europe –
271 Secondary Organic Aerosol Model (MADE/SORGAM) (Ackermann et al., 1998; Schell et al.,
272 2001) and the Volatility Basis Set (MADE/VBS) (Ahmadov et al., 2012). The CB05-VBS option
273 has also been coupled to existing model treatments including the aerosol direct effect, the aerosol
274 semi-direct effect on photolysis rates of major gases, and the aerosol indirect effect on CDNC and
275 resulting impacts on shortwave radiation. The physics options used in WRF/Chem include the
276 rapid and accurate radiative transfer model for GCM (RRTMG) for both shortwave and longwave
277 radiation, the Yonsei University (YSU) planetary boundary layer (PBL) scheme (Hong et al., 2006;
278 Hong, 2010), the Morrison et al. (2009) double moment microphysics scheme, as well as the Multi-
279 scale Kain-Fritsch (MSKF) cumulus parameterization scheme (Zheng et al., 2016). Aqueous-
280 phase chemistry module (AQCHEM) for both resolved and convective clouds is based on a similar
281 AQCHEM module in CMAQv4.7 of Sarwar et al. (2011). The anthropogenic emissions used are
282 from the 2010 emissions based on the 2008 U.S. Environmental Protection Agency (U.S. EPA)
283 National Emissions Inventory (NEI) from the Air Quality Model Evaluation International Initiative
284 (AQMEII) project (Pouliot et al., 2015). Dust emissions are based on the Atmospheric and
285 Environmental Research Inc. and Air Force Weather Agency (AER/AFWA) scheme (Jones and
286 Creighton, 2011). Emissions from sea salt are generated based on the scheme of Gong et al. (1997).

287 Biogenic emissions are simulated online by the Model of Emissions of Gases and Aerosols from
288 Nature v2.1 (MEGAN2.1) (Guenther et al., 2006).

289 The chemical initial and boundary conditions (ICONS/BCONs) come from the modified
290 CESM/CAM version 5.3 with updates by Gantt et al. (2014), He and Zhang (2014), and Glotfelty
291 et al. (2016). The meteorological ICONs/BCONs are from the National Center for Environmental
292 Protection Final Reanalyses (NCEP FNL) dataset, which is available every 6 hours. The chemical
293 fields are also allowed to run continuously while the meteorology is reinitialized every 5 days. The
294 simulations are performed at a horizontal resolution of 36-km with 148×112 horizontal grid cells
295 over the CONUS domain and parts of Canada and Mexico, and a vertical resolution of 34 layers
296 from the surface to 100-hPa.

297 A number of sensitivity simulations are designed to identify the model configuration with
298 results that are in the closest agreement to observations as well as the realistic model treatments of
299 OA that are the closest to atmospheric processes. The baseline and sensitivity simulations are
300 conducted from May to June 2010, during which the Nexus of Air Quality and Climate Change
301 (CalNex) campaign was held in Bakersfield and Pasadena, California. The first 10 days from May
302 1st to May 10th are considered to be the spin-up period.

303 **2.2. Model Evaluation Protocol and Available Measurements**

304
305 Statistical measures including the Mean Bias (MB), Correlation Coefficient (Corr),
306 Normalized Mean Bias (NMB) and Normalized Mean Error (NME) (Yu et al., 2006) are used to
307 evaluate the simulations against observational data. Observational data are available for organic
308 carbon (OC) and total carbon (TC) from the Speciated Trends Network (STN) and the Interagency
309 Monitoring for Protected Visual Environments (IMPROVE). While both OC and TC from
310 IMPROVE are used for model evaluation, only TC data from STN are used as STN uses the

311 thermo-optical transmittance protocol for OC that is different from the one used by IMPROVE
312 (Zhang et al., 2012). In addition, the measurements for STN OC are not blank corrected for carbon
313 on the background filter (Wang et al., 2012). The ratios OA/OC ratios vary across locations in the
314 continental U.S. (CONUS) depending on whether the OA is dominated by secondary formation
315 (Aitken et al., 2008) or it contains more aliphatic hydrocarbons (Turpin and Lim, 2001). In this
316 study, two ratios, 1.4 and 2.1, are used to convert simulated OA to OC based on a number of
317 [studies in](#) literature (Turpin and Lim, 2001; Aitken et al., 2008; Xu et al., 2015). As the simulations
318 are based on CONUS with varying OA properties (less or more oxidized OA), the use of two
319 OA/OC ratios can represent the different types of OA present for all locations in the U.S. Spatial
320 plots, time series plots at specific sites, as well as overlay plots are used to evaluate model
321 performance. The IMPROVE sites chosen for the time series plots include the visibility-protected
322 areas in Brigantine National Wildlife Refuge (NWR), NJ, Death Valley National Park (NP), CA,
323 Swanquarter National Wildlife Refuge (NWR), NC, and the Tallgrass Prairie National Preserve,
324 KS. The Brigantine NWR is a tidal wetland and has a shallow bay, the Death Valley NP is a desert,
325 and the Swanquarter NWR is a coastal brackish marsh. The time series plots are made at four STN
326 sites including two urban sites: in Washington, DC and Boise, ID, one industrial site in Tampa,
327 FL, and one rural/agricultural site in Liberty, KS. SOA, hydroxyl radical (OH) and hydroperoxy
328 radical (HO₂) data are also available for May to June 2010 as part of the California Research at the
329 Nexus of Air Quality and Climate Change (CalNex) campaign (Kleindienst et al., 2012;
330 Lewandowski et al., 2013) in Bakersfield, CA and Pasadena, CA, which are both urban locations.
331 The Bakersfield sampling site is located between the city center and areas of agricultural activity,
332 while the Pasadena site is located at the California Institute of Technology campus within the Los
333 Angeles metropolitan area to the southwest and mountains in the north (Baker et al., 2015).

334 POA/OA ratios are also used to evaluate the performance of the model. A number of studies
335 have reported observed POA/OA ratios which range from 15% to 40% over CONUS. For
336 example, over southeastern U.S., hydrocarbon-like OA (HOA) and cooking OA are found to
337 contribute to 21 – 38% of total OA in urban sites (Xu et al., 2015). HOA and oxygenated OA
338 (OOA) are found to account for 34% and 66% of measured OA from Pittsburgh in September 2002
339 (Zhang et al., 2005). HOA and cooking OA are assumed to be synonymous to POA, and OOA is
340 assumed to be synonymous to SOA. Particulate matter sampled during August and September
341 2006 in Houston as part of the Texas Air Quality Study II Radical and Aerosol Measurement
342 Project showed that approximately 32% of OA comes from HOA (Cleveland et al., 2012). Results
343 from positive matrix factorization analysis from the Pasadena ground site during May and June
344 2010 showed that the primary components contribute 29% of the total OA mass (Hayes et al.,
345 2013). Based on Zhang et al. (2007), the percentages of HOA mass at urban sites in Riverside,
346 CA, from mid-July to mid-August 2005, in Houston, TX, from mid-August to mid-September
347 2000, and in New York City in July 2001 are 15%, 38%, and 30%, respectively. In addition, Zhang
348 et al. (2011) compiled a large number of field campaigns across the globe where the average
349 POA/OA ratios for urban, downwind and rural/remote areas are found to be 0.42, 0.18 and 0.10
350 respectively.

351 For the aerosol activation sensitivity and production simulations, additional variables that will
352 be analyzed in this study include maximum 1-hour and 8-hour O₃ against the Clean Air Status and
353 Trends Network (CASTNET) and Air Quality System (AQS), aerosol optical depth (AOD),
354 CDNC and cloud condensation nuclei (CCN) against MODIS.

355 **3. Model Development and Improvement**

356

357 A number of modifications have been made to the standard version of WRF/Chem model
358 v3.7.1. Those modifications and treatments are described below.

359 **3.1. OA Treatments**

360
361 The CB05-VBS treatment in the default WRF/Chem v3.7.1 assumes that POA is nonreactive
362 and nonvolatile. In this study, POA is assumed to be semivolatile, and can undergo gas-particle
363 partitioning, similar to anthropogenic SOA (ASOA) and biogenic SOA (BSOA) in VBS. While
364 the volatility of ASOA and BSOA is represented by 4 bins with C^* from 10^0 to $10^3 \mu\text{g m}^{-3}$. The
365 POA is distributed into 9 bins, with C^* from 10^{-2} to $10^6 \mu\text{g m}^{-3}$, following the set-up of Shrivastava
366 et al. (2011). The POA is oxidized to form semi-volatile OA (SVOA), which can also undergo
367 gas-particle partitioning. For the POA, bin-resolved enthalpies of vaporizations are used, ranging
368 from 64 kJ mol^{-1} for the 9th bin to 112 kJ mol^{-1} for the 1st bin according to Shrivastava et al. (2011).
369 The default enthalpy of vaporization (ΔH_{vap}) for SOA in WRF/Chem is 30 kJ mol^{-1} according to
370 Lane et al. (2008). A more accurate alternative is to use the ΔH_{vap} values calculated from the semi-
371 empirical correlation from Epstein et al. (2010):

$$372 \quad \Delta H_{\text{vap}} = -11 \log_{10} C^*_{300} + 129 \quad (1)$$

373 The values of ΔH_{vap} Epstein et al. (2010) are used in a number of sensitivity simulations and final
374 production simulation.

375 Shrivastava et al. (2013, 2015) also implemented several cases of fragmentation and
376 functionalization (FF) processes into VBS. For this study, the FF set-up is similar to the method
377 employed by Shrivastava et al. (2013), with the exception that fragmentation percentages of 10%,
378 25%, and 50% are used in sensitivity simulations. Shrivastava et al. (2013) used fragmentation
379 percentages of 50% (intermediate fragmentation) and 85% (high fragmentation) in his simulations
380 over Mexico City. For example, for the 10% FF case, 10% of the mass in the VBS species is

381 functionalized and moved to the next lower volatility bin, 80% is fragmented and moved to the
382 highest volatility bin, and the remaining 10% is fragmented and becomes more volatile than the
383 highest volatility bin (i.e., it is lost from the current volatility bins). For the 50% FF case, 50% is
384 functionalized and moved to the next lower volatility bin, 40% is fragmented and moved to the
385 highest volatility bin, and 10% is lost.

386 Zhao et al. (2014) measured IVOCs in Pasadena, CA during CalNex and found that the
387 concentrations of primary IVOCs are similar to those of single-ring aromatics, and they produce
388 about 30% of newly formed SOA in the afternoon. With the semivolatile POA and FF cases in this
389 study, additional IVOC and SVOC emissions are added as three times of the traditional POA
390 emissions from NEI, to account for missing IVOC and SVOC species in the traditional POA
391 emission inventory. The fraction of IVOC/SVOC emissions assigned to each volatility bin is
392 summarized in Table 3.

393 The mass fraction of organics in each volatility bin determined in laboratory studies also differs
394 significantly according to the sources of organics. For example, May et al. (2013a, b, c) has
395 different volatility distributions of mass fractions of organics for gasoline vehicle exhaust, diesel
396 exhaust, and biomass burning. To take into account the different sources of organic compounds
397 into a single volatility distribution for the purpose of this work, a new volatility distribution is
398 calculated based on the mass fractions reported by Shrivastava et al. (2011), May et al. (2013a, c)
399 and the percentages of VOC emissions from various sources from the 2008 NEI. According to the
400 2008 NEI report (Rao et al., 2013), total VOC emissions from stationary, mobile and fire
401 (prescribed and wildfire) sources are ~7.6, ~5.6, and ~49.6 million tons, respectively. The
402 corresponding percentages for VOC emissions are ~12%, ~9%, and ~79% for stationary, mobile,
403 and fire sources, respectively. Based on the U.S. EPA (2013), the percentages of diesel emissions

404 from mobile sources are low compared to gasoline sources (~7% of total diesel and gasoline
405 sources); they are thus not included in this study.

406 An example calculation for the mass fraction of the lowest volatility bin for POA and
407 IVOC/SVOC emissions are as follows:

$$408 \quad \text{Log } C_{-2}^* \text{ (at 298K)} = 0.04 \times 12\% + 0.14 \times 9\% + 0.79 \times 79\% = 0.1754 \quad (2)$$

409 where C_{-2}^* refers to the lowest volatility bin with a value of $10^{-2} \mu\text{g m}^{-3}$, 12%, 9%, and 79% refer
410 to the percentages for VOC emissions from stationary, mobile, and fire sources, respectively from
411 NEI, 0.04 refers to the original mass fraction for stationary emissions based on anthropogenic
412 emissions from Shrivastava et al. (2011) for the lowest volatility bin with a value of $10^{-2} \mu\text{g m}^{-3}$,
413 0.14 refers to the original mass fraction for gasoline emissions from May et al. (2013a) for the
414 lowest volatility bin with a value of $10^{-2} \mu\text{g m}^{-3}$, 0.2 refers to the original mass fraction for biomass
415 burning emissions from May et al. (2013c) for the lowest volatility bin with a value of $10^{-2} \mu\text{g m}^{-3}$,
416 and 0.1754 refers to the newly-calculated mass fraction of POA and IVOC/SVOC emissions for
417 this study. The mass fractions used by Shrivastava et al. (2011), May et al. (2013a, c), and this
418 work can be found in Table 3.

419 **3.2. Gas-Phase Chemical Mechanisms**

420
421 Three gas-phase mechanisms are used: CB05, CB6, and SAPRC07. The gas-phase
422 mechanisms for CB6 and SAPRC07 are coupled to the MADE/VBS in WRF/Chem v3.7.1 in this
423 work following the coupling of CB05 with MADE/VBS by Wang et al. (2014). The emissions for
424 all cases are based on the CB05 chemical species from the 2010 emissions based on the 2008 NEI.
425 For SAPRC07, slight modifications had to be made to account for the different VOC species or
426 groups. The mapping of emission species from CB05 to SAPRC07 is based on the grouping of

427 species from emitdb.xls from Henderson et al. (2014) as well as from
428 <http://www.cert.ucr.edu/~carter/emitdb/old-emitdb.htm>. CB05 emissions are used for the CB6
429 case, with the exception of the VOCs including propane, benzene, ethyne, acetone, and ketone that
430 are mapped based on fractions of existing CB05 VOCs according to Yarwood et al. (2010).

431 In VBS, the SOA precursors for CB6 are similar to those for CB05. The SOA precursors for
432 CB05 (and therefore CB6) are mapped from the default SAPRC99 precursors by Wang et al.
433 (2015). The SAPRC07 SOA precursors follow the existing mapping of SAPRC99-MOSAIC/VBS
434 in WRF/Chem. The chemical equations and rate parameters from ENVIRON (2013) and Carter
435 (2010) for CB6 and SAPRC07 gas-phase mechanisms, respectively, were included in the
436 chem/KPP/mechanisms directory in WRF/Chem. The SAPRC07 gas-phase mechanism
437 implemented in WRF/Chem in this case is the uncondensed and expanded version C, which
438 includes reactions for peroxy radical operators (Carter, 2010). Species in both CB6-MADE/VBS
439 and SAPRC07-MADE/VBS undergo dry deposition, aqueous chemistry, photolysis, and wet
440 scavenging that are similar to CB05-MADE/VBS.

441 **3.3. Aerosol Activation**

442
443 The FN05 series aerosol activation parameterizations (with the exclusion of MN14) have been
444 incorporated into 3-D regional air quality models and global climate and Earth system models such
445 as the WRF-Community Atmosphere Model version 5 (WRF-CAM5) (Zhang et al., 2015), and in
446 the global-through-urban WRF/Chem (GU-WRF/Chem) (Zhang et al., 2012) and CESM (Gantt et
447 al., 2014). In this study, the FN series parameterizations are incorporated into WRF/Chem
448 following the methods of Gantt et al. (2014) and Zhang et al. (2015) as described in detail in Zhang
449 et al. (2015). However, in WRF/Chem, the aerosol activation module is only linked to the
450 microphysics module through the variable CDNC, which is read by the microphysics module. It

451 is not coupled to the cumulus parameterization scheme unlike in WRF-CAM5 and CESM. The
452 FN05 series has been incorporated into module_mixactivate.F in the physics directory in
453 WRF/Chem. As BN07 involves the entrainment effect for convective clouds and has very small
454 impacts on non-convective CDNC (Zhang et al., 2015), it is not included in this study. In addition,
455 unlike Gantt et al. (2014) and Zhang et al. (2015), the KU09 treatment is also not included in this
456 study as the empirical constants A_{FHH} and B_{FHH} used in the formulation, which are compound-
457 specific, have not been experimentally determined for black carbon, although those constants have
458 been determined for dust and confirmed by Laaksonen et al. (2016). The additional MN14
459 treatment incorporated in this study involves a small modification to the original FN05 series
460 parameterizations (without KU09), and helps to better account for the size of inertially limited
461 CCN, and to remove a discontinuity in the calculation of the surface area of cloud droplets
462 (Morales Betancourt and Nenes, 2014). The updated treatments are about 20% more
463 computationally expensive to run as compared to ARG00 (Zhang et al., 2016), but capture the
464 sensitivity of CDNC to all aspects of the aerosol with comparable accuracy to numerical parcel
465 models, which was shown to be an underlying reason for biases from ARG (Morales Betancourt
466 et al., 2014).

467 **4. Results and Discussions**

468

469 **4.1.Sensitivity Simulations with VBS Treatments Coupled with CB05**

470

471 As listed in Table 4, a number of sensitivity simulations are designed to identify the best model
472 configuration for OA treatments with the closest agreement to observations over CONUS. Those
473 sensitivity simulations consider (i) two SOA modules (MADE/SORGAM vs MADE/VBS), (ii)
474 two types of VBS treatment for POA (nonvolatile POA vs-versus semivolatile POA), (iii) two
475 ΔH_{vap} treatments (default vs-versus the semi-empirical ΔH_{vap} equation by Epstein et al. (2010)),

476 (iv) three different percentages of functionalization and fragmentation (FF) (10%, 25%, and 50%),
477 (v) three sets of POA emissions (default ~~vs.~~versus 1.5 or 3 times the original NEI POA emissions),
478 (vi) three different gas-phase mechanisms (CB05, CB6, and SAPRC07), and (vii) two different
479 aerosol activation schemes (ARG00 ~~vs.~~versus combinations of different aerosol activation
480 schemes of the FN05 series: FN05, FN05/BA10, and MN14) All simulations except for CB05-
481 SORG-DH contain the VBS treatments for OA. CB05-SORG-DH and CB05-VBS-DH treat POA
482 emissions as nonvolatile. In addition, the impact of two different cumulus parameterization
483 schemes: Grell – Freitas (Grell and Freitas, 2014) and the Multi-scale Kain Fritsch (MSKF) (Zheng
484 et al., 2016) scheme were also tested.

485 Table 5 summarizes the main statistics for all sensitivity simulations in terms of mean obs,
486 mean sim, Corr, NMB, and NME for hourly OC and TC concentrations against IMPROVE and
487 hourly TC concentrations against STN, respectively, over the whole CONUS domain. Figure 1
488 compares the domain mean hourly averaged observed OC or TC concentrations based on
489 IMPROVE and STN with simulated concentrations calculated based on the ratios of OA/OC 1.4
490 and 2.1 for each sensitivity simulation. The domain mean hourly averaged obs OC concentration
491 is $0.88 \mu\text{g m}^{-3}$ for IMPROVE, and the domain mean hourly averaged obs TC concentration is 1.03
492 $\mu\text{g m}^{-3}$ for IMPROVE and $2.71 \mu\text{g m}^{-3}$ for STN. As shown in Figure 1, the simulation
493 CB05_SORG_DH with the default SOA module SORG largely underpredicts OC and TC with the
494 largest NMBs and NMEs and the lowest Corr as compared to all other simulations with a SOA
495 module based on the VBS method. The remaining VBS simulations significantly reduce the biases
496 and errors in OC and TC from CB05_SORG_DH and also improve the correlation. Compared to
497 CB05_SORG_DH, CB05_VBS_DH with nonvolatile POA seems to perform relatively well in
498 terms of NMBs and Corr against IMPROVE OC, IMPROVE TC, and STN TC.

499 Adding the semivolatile POA treatment with 1.5 times the NEI POA emissions
500 (CB05_POA_DH) reduces simulated OC and TC concentrations as compared to CB05_VBS_DH,
501 due to the loss of mass from the semivolatile POA. As the POA mass is reduced, less surface area
502 is available for SOA precursors to condense onto, resulting in decreased OA (thus decreased OC
503 and TC) for CB05_POA_DH. Using the semi-empirical correlation of Epstein et al. (2010) for
504 ΔH_{vap} increases the OC and TC concentrations (CB05_POA ~~vs.~~versus CB05_POA_DH).
505 Compared to the default ΔH_{vap} of 30 kJ mol⁻¹ used in CB05_POA_DH, the semi-empirical
506 correlation of Epstein et al. (2010) gives much higher ΔH_{vap} values, resulting in more of the
507 organic vapors in the particulate phase than in the gas phase. Compared to CB05-POA, the
508 simulations with various FF treatments decrease the OA concentrations, as part of the OA mass is
509 fragmented to higher volatility bins. The 10% FF case (CB05_10% FF) does not differ significantly
510 from the no FF case (CB05_POA). However, increasing the percentage of FF (from 10% to 25%,
511 then to 50%) decreases the OA concentrations. The FF treatments, however, even if they are more
512 representative of actual SOA atmospheric formation processes, reduce the Corr slightly (compared
513 to the cases CB05_POA and CB05-10%FF). By doubling the POA emissions (from 1.5 to 3.0
514 times the original POA NEI emissions) for the 25% FF case (CB05_FF25%_EM3), the predicted
515 OC and TC concentrations are closer to the observations. When evaluated against IMPROVE OC,
516 IMPROVE TC, and STN TC, among for simulations using CB05, the simulations
517 CB05_VBS_DH, CB05_POA, CB05_FF10%, and CB05_FF25%_EM3 perform better than other
518 cases. The differences in the OC and TC predictions from the simulations with different gas-phase
519 mechanisms will be discussed later in Section 2.

520 Figure 2 shows the spatial distributions of simulated OC and TC concentrations overlaid with
521 observed OC from IMPROVE and TC from STN for the case CB05_25%FF_EM3 for the two

522 OA/OC ratios. The model performs much better for IMPROVE OC with an OA/OC ratio of 2.1
523 as compared to 1.4, especially over eastern U.S. where the use of an OA/OC ratio of 1.4 results in
524 large overpredictions. However over the central U.S. and parts of the western U.S., the use of an
525 OA/OC ratio of 1.4 shows slightly better predictions of IMPROVE OC compared to the use of
526 OA/OC ratio of 2.1 that gives underpredictions of OC. On the other hand, the model performs
527 better for STN OC with an OA/OC ratio of 1.4 as compared to 2.1. The use of an OA/OC ratio of
528 1.4 gives better agreement with STN TC over eastern U.S. where the use of an OA/OC ratio of 2.1
529 results in large underpredictions of TC. Evaluation of OC and TC against IMPROVE and STN,
530 respectively, therefore depends heavily on the OA/OC ratio, which is site-specific. Therefore in
531 more rural sites (IMPROVE), the OA/OC ratio is more likely to be high (~2.1) with more
532 oxygenated OA, while in more urban sites (STN), the OA/OC ratio is more likely to be lower
533 (~1.4) due to fresher emissions and less oxidized species.

534 Figure 3 shows the POA/OA ratios for six sensitivity simulations. As mentioned earlier, the
535 observed ratio of POA/total OA is approximately 15% to 40% during the summer period over
536 various locations in the CONUS. As SOA concentrations from field campaigns are sparse at
537 different locations and at different time periods, the POA/OA ratio is used to evaluate the model's
538 capability to reproduce POA and SOA concentrations. The simulation CB05_SORG_DH with
539 default SORGAM SOA module largely overpredicts the POA/OA ratio, due to significant
540 underpredictions of SOA. The simulations CB05_VBS_DH, CB05_50%FF, and
541 CB05_25%FF_EM3 with various VBS treatments all have POA/OA ratios that fall within the
542 range of 0.15 to 0.4, with lower POA/OA ratios over more rural areas and higher POA/OA ratios
543 over urban areas. CB05_VBS_DH, however, might give too high POA concentrations over the
544 western portion of the domain as it does not consider POA to be semivolatile. Considering

545 semivolatile POA, however, without considering the fragmentation and functionalization
546 processes in the simulation CB05_POA results in too low POA/OA ratio (< 0.1 over most areas).
547 Similarly, the CB05_FF25% case also results in a large portion of CONUS with POA/OA ratios
548 of < 0.1 , due to the loss of POA mass. CB05_FF50%, however, predicts reasonable POA/OA
549 ratios, even with fragmentation/functionalization due to balanced loss of both POA and SOA mass
550 through fragmentation to higher volatility bins. The simulation CB05_FF25%_EM3 also improves
551 from CB05_FF25% by increasing the POA mass contributing to higher POA/OA ratios.

552 Figure 4 shows the observed and simulated temporal variations of SOA concentrations at the
553 two CalNex sites: Bakersfield and Pasadena in CA from May to June 2010 for the simulations
554 CB05_SORM_DH, CB05_VBS_DH, CB05_25%FF_EM3, CB6_25%FF_EM3, and
555 SAPRC07_25%FF_EM3. There are large underpredictions of SOA by all runs on some days (e.g.
556 May 15 – 16, June 2 – 6, June 13 – 14) likely due to missing SOA precursor emissions. Table 6
557 shows the statistics of the simulations presented in Figure 4. The results using CB6 and SAPRC07
558 gas-phase mechanisms will be discussed in section 4.2. The observed SOA was derived based on
559 the tracer method of Kleindienst et al. (2012) which contains some uncertainties, and also likely
560 contributeds to the poor correlation for most of the cases. For example, it assumes mass fraction
561 of the tracers in secondary organic carbon is the same in the field as that in the laboratory, and the
562 tracers are assumed to be inert and are unlikely to undergo oxidation in the atmosphere, which
563 might not be the case. In addition, the SOA data from the CalNex campaign only consider
564 contributions from a small number of precursors including biogenic precursors (i.e., isoprene, α -
565 pinene, and β -caryophyllene), and the anthropogenic precursors (i.e., toluene, polycyclic aromatic
566 hydrocarbons (PAHs) and methyl butenol (MBO)).

567 As shown in Figure 4 and Table 6, the simulation CB05_SORG_DH with the default
568 SORGAM SOA module significantly underpredicts observed SOA concentrations at both sites.
569 The model configuration of CB05_VBS_DH has been used in a number of WRF/Chem
570 simulations published in literature (e.g., Yahya et al., 2015a; Campbell et al., 2015; Wang et al.,
571 2015a, b). At Bakersfield, the simulation CB05_VBS_DH overpredicts the SOA concentrations
572 for almost all the days. The simulation CB05_25%FF_EM3, however, underpredicts the SOA
573 concentrations at Bakersfield, especially in June. The CB05_25%FF_EM3 case also shows low
574 SOA concentrations throughout May and June, without much variability in SOA concentrations,
575 likely due to underestimations of original POA emissions at Bakersfield. As the S/IVOC emissions
576 for CB05_25%FF_EM3 are a factor of 3 of the original POA emissions from NEI, if the original
577 POA emissions from NEI are underestimated, the S/IVOC emissions will be low, resulting in low
578 SOA concentrations due to low concentrations of condensable material. At Pasadena, both
579 CB05_VBS_DH and CB05_25%FF_EM3 overpredict the obs SOA from May 15th to May 30th,
580 but are unable to capture the high SOA concentrations from 2nd to 6th June. The CB05_VBS_DH
581 case seems to perform better than the CB05_25%FF_EM3 case when observed SOA
582 concentrations are high. The results from this study are consistent with those from Baker et al.
583 (2015), which showed that measured PM_{2.5} OC at Bakersfield is largely underpredicted compared
584 to Pasadena. Baker et al. (2015), however, attributed to the underpredictions of OC at Bakersfield
585 and Pasadena mainly to primary OC predicted by the baseline model, as compared to the Aerosol
586 Mass Spectrometer measurements, suggesting that OC is mostly secondary in nature in Pasadena.
587 In addition, as mentioned earlier, the simulated SOA from WRF/Chem does not consider
588 contributions from all the SOA precursors identified by their trace compounds (e.g., the biogenic
589 precursor, b-caryophyllene, and the anthropogenic precursor MBO, are not included in

590 WRF/Chem), which can help to account for the discrepancies between the simulated and observed
591 SOA concentrations.

592 4.2. Sensitivity of OA predictions to different gas-phase mechanisms

593

594 Figure 1 shows that CB05_FF25%_EM3 produces the highest OC and TC concentrations at
595 the IMPROVE sites, followed by CB6_FF25%_EM3 and SAPRC07_FF25%_EM3, while
596 CB6_FF25%_EM3 produces the highest TC concentrations at the STN sites. However, the
597 differences in domain-mean simulated OC and TC between the simulations with the three different
598 gas-phase mechanisms are small, compared to the differences in simulated OC and TC due to
599 differences in VBS treatments (e.g., nonvolatile ~~vs.~~versus semivolatile POA). Figure 4 also shows
600 that there are not much differences between simulated SOA concentrations with different gas-
601 phase mechanisms at Bakersfield, but larger differences are found at Pasadena. . For example,
602 SAPRC07_25%FF_EM3 produces much higher SOA concentrations compared to
603 CB05_25%FF_EM3 and CB6_25%FF_EM3 at Pasadena on several days (e.g., June 6-8). Figure
604 5 shows the time series of hydroxyl radical (OH) mixing ratios as well as diurnal plots of OH and
605 hydroperoxyl radical (HO₂) at Pasadena from the CalNex field campaign. The time series of HO₂
606 is not shown due to irregularity of the observational data. The model is able to reproduce the
607 diurnal variation of OH radicals but significantly overpredicts the daytime and peak OH mixing
608 ratios, especially for CB05 and CB6. All gas-phase mechanisms underpredict OH mixing ratios at
609 night. Among all simulations, SAPRC07 produces the closest simulated OH mixing ratios
610 compared to CB05 and CB6 gives the largest overpredictions. Similarly, the HO₂ mixing ratios
611 are generally overpredicted by all gas-phase mechanisms with SAPRC07 performing the best. The
612 overpredictions in OH and HO₂ mixing ratios do not help explain the underpredictions of SOA for

613 several days at Pasadena where underpredictions of VOCs may be the main cause, which is
614 consistent with the findings of Baker et al. (2015).

615 Figure 6 shows spatial distributions of average concentrations of oxidants including ozone
616 (O_3), OH, HO_2 , as well as the OA species including anthropogenic SOA (ASOA), biogenic SOA
617 (BSOA), TSOA, and POA. SAPRC07-25%FF-EM3 produces the highest domain average O_3
618 mixing ratios but the lowest domain average OH+ HO_2 mixing ratios while CB6-25%FF-EM3
619 produces the highest domain average and maximum OH+ HO_2 mixing ratios but the lowest domain
620 average O_3 mixing ratios. These findings are mostly consistent from literature. For example,
621 maximum O_3 and OH mixing ratios over the Los Angeles area are higher for CB6 compared to
622 CB05, which are consistent with the results from Yarwood et al. (2010). SAPRC07 also generally
623 produces higher O_3 mixing ratios compared to CB05. However, average O_3 mixing ratios from
624 CB6 are expected to be higher than CB05 (rather than lower as shown in Figure 6), according to
625 the study from Nopmongcol et al. (2012) which showed higher O_3 mixing ratios over Europe for
626 January and July using the Comprehensive Air Quality Model with Extensions (CAMx). CB6 is a
627 relatively new gas-phase mechanism, there are very few studies that evaluated its performance
628 over a longer period of time, e.g., for the whole summer, and over CONUS. In addition, there are
629 other uncertainties in this study. For example, the emissions for CB05 are used for CB6, the
630 additional explicit VOC species in CB6 such as benzene and acetylene are not considered, which
631 can also contribute to O_3 formation. In addition, most locations in the U.S. in 2010 are considered
632 to be NO_x -limited with localized VOC-limited regimes from May to September (Campbell et al.,
633 2015), which means that O_3 formation is more likely to depend on NO_x rather than VOC
634 concentrations.

635 Table 7 shows the statistics for maximum 1-hr and 8-hr O₃ mixing ratios evaluated against
636 CASTNET and AQS. CASTNET sites are mainly rural sites, while AQS consists of urban,
637 suburban, and rural sites. As expected, SAPRC07 consistently produces the highest maximum 1-
638 hr and maximum 8-hr O₃ mixing ratios and overpredicts at AQS sites with an NMB of ~16%.
639 However, SAPRC07 performs the best at CASTNET sites, as both CB05 and CB6 significantly
640 underpredict maximum 1-hr and maximum 8-hr O₃ mixing ratios. At CASTNET sites, CB6
641 performs the poorest with the largest underpredictions for both maximum 1-hr and 8-hr O₃ mixing
642 ratios. However, CB6 predicts higher maximum 1-hr and 8-hr O₃ mixing ratios at AQS sites, while
643 CB05 predicts the lowest maximum 1-hr and 8-hr O₃ mixing ratios at AQS sites. It is likely that
644 CB6 predicts higher O₃ mixing ratios at more VOC-limited sites in urban areas, while CB05
645 predicts higher O₃ mixing ratios at more NO_x-limited areas, due to the improvement in VOC
646 speciation in CB6 compared to CB05. Overall, however, CB05 has the highest Corr and the lowest
647 NMEs for CASTNET maximum 1-hr and AQS maximum 1-hr and 8-hr O₃ mixing ratios. For
648 PM_{2.5} concentrations, CB6 produces the best performance against IMPROVE (highest Corr,
649 lowest NMB and NME) while CB05 produces the best performance against STN (highest Corr
650 and lowest NME). All 3 cases perform poorly for PM₁₀ against AQS, with large underpredictions
651 due to the non-consideration of the coarse mode inorganic species in MADE-VBS treatments.

652 Anthropogenic SOA (ASOA) concentrations are lower for CB6 and SAPRC07 compared to
653 CB05. This is likely partially due to the emissions which are mapped from CB05 to CB6 and
654 SAPRC07. The CB05 emissions are not likely to account for all anthropogenic VOC emissions in
655 CB6 and SAPRC07, resulting in lower ASOA concentrations for CB6 and SAPRC07 compared
656 to CB05. Biogenic SOA (BSOA) concentrations, however, are the largest for CB6, followed by
657 SAPRC07 and CB05. BSOA concentrations are likely the highest for CB6 due to the highest

658 OH+HO₂ mixing ratios for CB6. The more extensive VOC representation and high O₃ mixing
659 ratios for SAPRC07 also likely contribute to the high BSOA concentrations for SAPRC07
660 compared to CB05. However, overall, the total SOA (TSOA) and POA concentrations for all three
661 gas-phase mechanisms do not vary much, resulting in similar OA concentrations.

662 Figures 7 and 8 show the time series of simulated ~~versus~~, observed OC from IMPROVE and
663 simulated ~~vs~~, versus observed TC from STN at several representative sites over CONUS for the
664 different gas-phase mechanisms. In general, at IMPROVE sites, CB05 gives the highest OC
665 concentrations compared to CB6 and SAPRC07 most of the time, resulting in overpredictions of
666 OC concentrations, while CB6 and SAPRC07 perform better against IMPROVE OC. The
667 overpredictions of CB05 are likely due to overpredictions in ASOA (as CB05 produces the highest
668 ASOA concentrations compared to CB6 and SAPRC07 as shown in Figure 6). As these sites are
669 located in rural locations, the dominant SOA is likely to be BSOA, or downwind ASOA from more
670 urban areas. With the exception of Death Valley NP, CA, the model performs relatively well in
671 predicting IMPROVE OC concentrations. Simulations with all three gas phase mechanisms
672 overpredict OC concentrations over several days in May in Brigantine NWR, Death Valley and
673 Swanquarter, but is able to predict several of the peaks in June. All three gas-phase mechanisms,
674 however, largely underpredict OC concentrations over Death Valley from May 21st to June 30th.
675 As the Death Valley NP is a desert, the OC at Death Valley NP is most likely due to downwind
676 OC transported from upwind locations, for which the model is not able to capture due to
677 meteorological biases such as biases in wind fields. The differences between simulation results
678 from the gas-phase mechanisms are smaller for STN TC compared to IMPROVE OC, probably
679 due to similar elemental carbon (EC) concentrations for all gas-phase mechanisms, which can form
680 a significant percentage of TC. In general, all simulations with the three gas-phase mechanisms

681 also show similar trends (peaks and troughs) for simulated TC, likely due to influences from
682 meteorological parameters such as wind and precipitation. Overall, all three simulations are also
683 able to predict the magnitude and trends of STN TC concentrations relatively well. Similarly,
684 CB05 tends to produce the highest TC concentrations, however, CB6 also does produce the highest
685 TC concentrations for several days, for example, for some days in May in Washington, DC and
686 Tampa, FL, as well as in June in Liberty, KS, likely due to influences of BSOA where CB6
687 produces the highest concentrations as shown in Figure 6.

688 **4.3. Impact of Different VBS treatments on CDNC**

689
690 Table 7 shows the statistics for model evaluation for simulated CDNC against MODIS-derived
691 CDNC from Bennartz (2007) for May to June 2010. All simulations underpredict CDNC due likely
692 to underpredictions in PM and CCN concentrations and uncertainties and/or assumptions in the
693 derived CDNC based on MODIS retrievals of cloud properties by Bennartz (2007) (Zhang et al.,
694 2015). For example, Bennartz (2007) derived the CDNC from cloud optical depths and cloud
695 effective radius assuming adiabatically-stratified clouds. Among all simulations with CB05,
696 CB05_SORG_DH produces the lowest CDNC due to underestimated OA concentrations.
697 Increasing the OA concentrations helps to reduce the negative biases for CDNC. There are small
698 differences, however, among simulated CDNC with different VBS treatments for CB05 in CDNC
699 predictions, with similar Corr \sim 0.29, NMBs of \sim -29% to -27% and NMEs of \sim 47%. Figure 9
700 shows the spatial differences in predictions in warm clouds between the several simulations and
701 the simulation CB05_VBS_DH. CB05_SORGAM_DH gives the lower CDNC than
702 CB05_VBS_DH, indicating that the VBS treatment in CB05_VBS_DH helps to increase CDNC
703 significantly. While other simulations with semivolatile POA treatments further increase domain
704 average CDNC comparing to CB05_VBS_DH, the differences between CDNC predictions from

705 those simulations and CB05_VBS_DH are quite similar. In general, CDNC with the semivolatile
706 POA cases are higher over western U.S. but lower over eastern U.S. due to decreases in column
707 OA concentrations for the semivolatile POA cases compared to CB05_VBS_DH over eastern U.S.

708 The large differences in CDNC predictions, however, are found between simulations with the
709 different gas-phase mechanisms. SAPRC07_25%FF_EM3 has the largest negative bias (NMB of
710 -52%) compared to all other simulations with CB05 and the simulation with CB6. Figure 10
711 compares the spatial plots for CDNC predictions for simulations with different gas-phase
712 mechanisms, as well as the surface spatial plots for total OA and inorganic PM_{2.5} concentrations.
713 The simulation with SAPRC07 shows significantly lower CDNC over northeastern U.S.
714 comparing to CDNC predictions from the other two simulations. While all three simulations show
715 similar total OA concentrations, large differences are found for their total inorganic PM_{2.5}
716 concentrations, with SAPRC07 producing the lowest domain mean and maximum total inorganic
717 PM_{2.5} concentrations. Compared to CB05 and CB6, the lower inorganic PM_{2.5} concentrations
718 simulated with SAPRC07 are likely due to the low OH+HO₂ mixing ratios for SAPRC07 as shown
719 in Figure 6, resulting in a lower PM number concentration and lower cloud condensation nuclei
720 (CCN), thus lower CDNC.

721 **4.4.Sensitivity Simulations for Aerosol Activation Parameterizations**

722
723 Among all OA sensitivity simulations, the simulation CB05-25%FF-EM3 gives an overall best
724 performance in terms of OC, TC, O₃, PM_{2.5}, and CDNC evaluation, it is thus selected to test various
725 aerosol activation parameterizations. As listed in Table 4, four sensitivity simulations are designed
726 to test the FN05 series aerosol activation parameterizations with improved treatments comparing
727 to the default ARG00 aerosol activation parameterization. These sensitivity simulations include
728 the default ARG00, the FN05, the combination of FN05 and BA10, and the MN14. These

729 simulations use the MSKF scheme instead of the Morrison microphysics schemes in the previous
730 SOA runs as the MSKF scheme has a better correlation with MODIS CDNC as compared to the
731 Morrison microphysics scheme. Table 8 summarizes the model evaluation results against MODIS-
732 derived CDNC from Bennartz (2007). The simulation ARG00 underpredicts CDNC with an NMB
733 of -35%. The FN05 series helps to reduce the underpredictions of CDNC significantly, because
734 they in general give higher activation fractions compared to the ARG00 parameterization under
735 most atmospheric conditions (Ghan et al., 2011). The addition of BA10 to the FN05 takes into
736 account the effects of condensation on giant CCN, which reduces the CDNC predictions and leads
737 to a negligible underprediction of CDNC (with an NMB of -0.8%) compared to a slight
738 overprediction by the FN05 with an NMB of 7.1%. MN14, which revises the original population
739 splitting method in FN05 and BA10, slightly increases the CDNC to an NMB of 4.2% comparing
740 to the FN05/BA10 simulation. The trends in the predictions of FN05, BA10, and MN14 are
741 consistent with the reported bias of $\sim+8\%$, -10% and -3% , respectively, by Morales Betancourt
742 and Nenes (2014) against the CDNC concentrations simulated from the cloud parcel model.
743 However, the Corr and NME are worse with the FN05 series and MN14. The NMEs are almost
744 doubled for the FN05 series and MN14, compared to that from the default ARG00. Figure 11
745 compares the spatial distributions of the simulated CDNC in warm clouds from ARG00, FN05
746 series, and MN14 and the MODIS-derived CDNC from Bennartz (2007). As shown in Figure 11,
747 the lower Corr and higher NMEs for the FN05 series as compared to ARG00 shown in Table 9, as
748 compared to ARG00, are due to the large overpredictions over northeastern U.S. but
749 underpredictions over other parts of the domain. The simulated CDNC from the default ARG00
750 case is similar to that from Bennartz (2007) over eastern U.S., the underpredictions are mainly
751 over western U.S. and over the ocean because of the known bias when large CCN are not present

752 (Morales Betancourt et al., 2014). The simulations with the FN05 series increase CDNC where
753 CCN is high, i.e., over the northeastern U.S., resulting in overpredictions in CDNC over
754 northeastern U.S., and does not help to improve CDNC predictions over other parts of the U.S. as
755 well as over the ocean.

756 Figure 12 compares the simulated CCN and AOD from the CB05_25%FF_EM3 + MN14 case
757 with those derived from the MODIS. The model largely underpredicts CCN, especially over the
758 western part of the domain, which explains the large underprediction of CDNC also over the
759 western part of the domain. Condensation of the available water vapor occurs over CCN which are
760 concentrated over northeastern U.S., resulting in overpredictions of CDNC over northeastern U.S.
761 The lack of CCN over the ocean and the western part of the domain is related to the
762 underpredictions of AOD over the same areas. This indicates biases in number (and probably mass)
763 concentrations of column PM concentrations, especially over the ocean and western U.S. PM_{2.5}
764 and PM₁₀ observational data are available over the surface and are both underpredicted, however,
765 there are no observational data for column concentrations of PM_{2.5} and PM₁₀ for evaluation.
766 Improving the spatial distribution and magnitude of emissions for PM species and precursors for
767 the model layers at the surface and above the surface can help improve AOD and CCN predictions,
768 therefore CDNC predictions.

769 **5. Summary and Conclusions**

770
771 Current regional air quality models including WRF/Chem have large uncertainties in modeling
772 OA and aerosol-cloud feedback mechanisms such as the aerosol activation process. Comparing to
773 the traditional OA method, the VBS treatment helps to improve OA predictions by reducing the
774 underpredictions of OA. By including a semivolatile POA treatment, using a semi-empirical
775 formation of Epstein et al. (2010) for ΔH_{vap} , including 25% fragmentation and functionalization

776 as well as including additional S/IVOC emissions, the VBS treatment in WRF/Chem simulates the
777 atmospheric OA formation processes more realistically and can perform relatively well in
778 predictions of OC and TC against IMPROVE and STN. POA/OA ratios for the
779 CB05_25%FF_EM3 and CB05_FF50% treatments are within the range of POA/OA ratios of
780 ~0.15 to 0.40 from literature. Compared to the simulation with default SORGAM SOA module,
781 the simulations with various new VBS treatments also give better agreement with observed SOA
782 at Bakersfield and Pasadena during the CalNex field campaign from May to June 2010. However,
783 biases exist in those simulations with the VBS treatments due to several possible reasons, including
784 underestimated POA emissions, underpredicted VOC concentrations, as well as differences in the
785 SOA precursors used in the model and those contributing to the observed SOA concentrations.
786 The simulations with different gas-phase mechanisms (i.e., CB05, CB6, and SAPRC07) produce
787 in general different ASOA and BSOA concentrations. SAPRC07 produces the highest O₃ mixing
788 ratios, while CB6 produces the lowest OH + HO₂ mixing ratios. CB6 also performs the best when
789 evaluated against IMPROVE PM_{2.5} while CB05 performs the best when evaluated against STN
790 PM_{2.5} concentrations. All 3 cases perform poorly against AQS PM₁₀ evaluation. Due to the
791 significant differences between O₃, OH, and HO₂ mixing ratios for the three gas-phase
792 mechanisms, inorganic PM concentrations vary widely, especially between the carbon bond
793 mechanisms (CB05 and CB6) and SAPRC07, resulting in significantly different predictions of
794 CDNC. The CDNC predictions do not vary much among simulations with CB05 and different
795 VBS treatments, for example, for simulations with nonvolatile ~~vs.~~versus semivolatile POA, and
796 with and without fragmentation and functionalization treatments. The simulation with SAPRC07
797 produces the lowest CDNC compared to those with CB05 and CB6, due to the lowest inorganic
798 PM number and mass concentrations resulted from the lowest OH and HO₂ mixing ratios among

799 all simulations. CB05 gives the best performances when evaluated against CASTNET and AQS
800 ozone mixing ratios, STN PM_{2.5} concentrations and against MODIS CDNC.

801 With the default ARG00 treatment in the model, in general, all simulations with VBS
802 treatments underpredict the MODIS-derived CDNC by Bennartz (2007). By including the FN05
803 series (i.e., FN05, FN05/BA10, and MN14), the underpredictions for CDNC are greatly reduced.
804 However, the correlation coefficient and errors are worse with the FN05 series, with large
805 overpredictions over the northeastern U.S., where CCN is high. The model performs poorly for
806 AOD and CCN, likely due to inaccuracies in spatial distribution and magnitudes of PM and PM
807 precursor emissions in the model layers at the surface and above the surface. The CDNC
808 predictions can be improved by improving AOD and CCN underpredictions over western U.S. and
809 over the ocean.

810 **Code and Data Availability**

811 The WRF/Chem v3.7.1 code used in this paper will be available upon request. The inputs
812 including the meteorological files, meteorological initial and boundary conditions, chemical initial
813 and boundary conditions, model setup and configuration, and the namelist setup and instructions
814 on how to run the simulations for a 1-day test case, as well as a sample output for a 1-day test, can
815 be provided upon request.

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817
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Tables

Table 1. Summary of several literature studies of VBS treatments in various regional and global models.

Source	Ahmadov et al., 2012	Shrivastava et al., 2011	Farina et al., 2010	Jathar et al., 2011	Hodzic et al., 2010
Model	WRF-Chem	WRF-Chem	GISS II' GCM	GISS II' GCM	CHIMERE
Domain	CONUS	Mexico City	Global	Global	Mexico City
Spatial Resolution	20 km and 60 km	Nested 3 km within 12 km	4° × 5°	4° × 5°	5 km × 5 km and 35 km × 35 km
Emissions of SVOCs, IVOCs, and VOCs	Only VOCs; no emissions of SVOCs and IVOCs	SVOC emissions 3 times POA emissions for both anthropogenic and biomass burning emissions. IVOC emissions 1.5 times POA emissions	POA is treated as nonvolatile and nonreactive, but acts as absorbing phase for SOA condensation, forming 1 OA phase	SVOC emissions are represented by the traditional emission inventory. IVOC emissions are 1.5 times traditional emissions	SVOC emissions 3 times POA emissions. IVOC emissions 1.5 times POA emissions
No. of VBS bins	4	2 and 9	4	9	9
Aging	Yes and No Simulations with aging: each oxidation step produces 7.5% additional mass	Yes and No Simulations with aging: each oxidation step produces 15% additional mass	Yes	Yes and No. Each oxidation step does not produce any additional mass	Yes. 2 cases below: (i)Each oxidation step produces 7.5% additional mass (ii)Each oxidation step reduces the volatility by 2 orders of magnitude and 40% of additional mass produced
Observational data	SEARCH, STN, IMPROVE	MILAGRO 2006 field campaign	IMPROVE, EMEP	IMPROVE, FAME, MILAGRO, SOAR	MILAGRO 2006 field campaign
Variables evaluated	OC and EC	OA, HOA, OOA O:C ratio	OM:OC of 1.8	OA (surface), HOA, OOA	HOA, OOA, BBOA, O:C ratio
Summary of results with VBS framework with/without aging compared to the traditional SOA approach	-Improved diurnal variability -Results without the aging process underestimate OC throughout the day	-HOA and OOA: Lower negative bias with addition of S/IVOC emissions -OOA: 2 bin VBS better results than 9 bin VBS -Underprediction of O:C ratio in both cases	-IMPROVE: improved with aging -EMEP: aging further biases already high OA predictions	-Adding IVOC emissions improves performance, however underprediction remains in winter months	-HOA overpredicted during nighttime -Case(i): Modeled O:C 3 times lower than observed -Case(ii): Better agreement for O:C but SOA generally overestimated

Note: HOA: Hydrocarbon-like OA – Reduced specie of OA, generally understood as a surrogate for urban combustion-related POA; OOA: Oxygenated OA – Characterized by its high oxygen content and generally understood as a surrogate for SOA; BBOA: Biomass burning OA

Table 1. (cont). Summary of several literature studies of VBS treatments in various regional and global models.

Source	Bergstrom et al., 2012	Lane et al., 2008	Donahue et al., 2009	Murphy et al., 2009	This work
Model	EMEP	PMCAMx	PMCAMx	PMCAMx	WRF/Chem
Domain	Europe, a large part of the North Atlantic and Arctic areas	Eastern U.S.	Eastern U.S.	Eastern U.S.	CONUS with parts of Canada and Mexico
Spatial Resolution	50 km × 50 km	36 km × 36 km	NA	36 km × 36 km	36 km × 36 km
Emissions of SVOCs, IVOCs and VOCs	VOCs are present. S/IVOCs are 2.5 times the POA emissions	Only VOCs; SVOCs and IVOCs not added	Additional IVOCs added but details are not given	IVOC emissions are 0.2 to 0.8 times the nonvolatile POA emission rates	S/IVOCs are 1.5 to 3 times the nonvolatile POA NEI emissions
No. of VBS bins	4 for SOA components and 9 for POA	4	9	10	4 for SOA components and 9 for POA
Aging	Yes and No. Each oxidation step produces 7.5% additional mass	Yes. No additional mass produced for each oxidation step.	Yes. No additional mass produced for each oxidation step.	Yes. No additional mass produced for each oxidation step.	Yes. Each oxidation step produces 7.5% additional mass
Observational data	CARBOSOL, SORGA, Gote-2005	STN, IMPROVE	NA	STN, IMPROVE	STN, IMPROVE, field data
Variables evaluated	TC, OC	OA	POA, OPOA, SOA	OA	TC, OC, POA/OA
Summary of results with VBS framework with/without aging compared to the traditional SOA approach	-Addition of aging reactions improve summertime results but has little or negative consequences in wintertime -Deteriorations of model results with increased aging at urban influenced sites in southern Europe	-Addition of aging reactions overpredicts the OA concentrations in rural IMPROVE stations but improves the model performance in urban areas	-Aging results in better model predictions	-Slight overprediction with IMPROVE -Underprediction with STN	-Large improvements in predictions

Note: TC: total carbon; OC: Organic carbon; OPOA: oxidized POA

Table 2. Summary of main characteristics of CB05, CB6, and SAPRC07 gas-phase mechanisms.

	CB05-CI¹	CB6	SAPRC07²
No. of species	70	114	118
No. of reactions	156	218	599
Lumping method	Lumped structure based on carbon bonds	Lumped structure based on carbon bonds	Lumped species based on their reactivity towards hydroxyl (OH)
Kinetic Data for rate constants	Mostly from IUPAC (Atkinson et al., 2005). NASA/JPL (Sander et al., 2003) values were used in some cases where IUPAC data was not available.	New information from IUPAC (Atkinson et al., 2010) and NASA (Sander et al., 2006)	Mainly from IUPAC (2006) and NASA (Sander et al., 2006).
Photolysis data	Mainly from SAPRC99 chemical mechanism. IUPAC (Atkinson et al., 2005) was used if it differs significantly from SAPRC99.	New information from IUPAC (Atkinson et al., 2010) and NASA (Sander et al., 2006)	Mainly from IUPAC (2006) and NASA (Sander et al., 2006).
Ozone chemistry	Slightly underpredict O ₃ mixing ratios with isoprene and in synthetic urban mixtures in chamber experiments.	Reduced underprediction in O ₃ mixing ratios from benzene, toluene, and xylene, but forms O ₃ from isoprene too slowly compared to CB05.	Slightly underpredict O ₃ mixing ratios at low NO _x levels in chamber experiments.
Organic nitrate	2 reactions involving organic nitrate (NTR).	Additional NO _x recycling from organic nitrate to represent fate of NO _x over multiple days.	Added peroxy+NO reactions to form organic nitrate.
Chlorine chemistry	20 additional reactions for Cl chemistry involving species Cl ₂ , HOCl, Cl, ClO, and FMCl.	CB05 chlorine chemistry included in this work.	22 base chlorine reactions involving CL ₂ , CLNO, CLONO, CLNO ₂ , CLONO ₂ , HOCl, and 26 additional reactions involving organic products
Organic chemistry	- Explicit organic aerosol precursors, e.g., isoprene, toluene, xylene, α -pinene, β -pinene.	- Explicit long-lived and abundant organic compounds including propane, acetone, benzene and acetylene added - Extensive revision of isoprene and aromatics chemistry - Formation of alpha-dicarbonyl compounds (glyoxal, glycoaldehyde, methylglyoxal) - Updates to peroxy radical chemistry that will improve formation of H ₂ O ₂	- Reformulated reactions of peroxy radicals so that effects of changes in NO _x conditions on organic product formation is more accurately represented - Most comprehensive representation of VOCs compared to other gas-phase mechanisms
3-D host models	Implemented into WRF/Chem v3.6.1 by Wang et al. (2014). Also available in WRF/Chem v3.7.1	Implemented in CAMx by ENVIRON (2013)	Implemented in CMAQ (Carter, 2010)
Reference	Yarwood et al. (2005)	Yarwood et al. (2010) ENVIRON (2013)	Carter (2010)

¹ CB05 gas-phase mechanism with reactive chlorine chemistry (Yarwood et al., 2005)

² SAPRC07 uncondensed and expanded version C, which includes reactions for peroxy radical operators (Carter, 2010).

Table 3. Factors to calculate S/IVOC emissions from POA emissions from Shrivastava et al. (2011), May et al. (2013a, c) and newly calculated factors for this study.

Log C_i^* at 298K	Normalized fraction for stationary emissions based on anthropogenic emissions from Shrivastava et al. (2011)	Fraction for gasoline emissions from May et al. (2013a)	Fraction for biomass burning emissions from May et al. (2013c)	New calculated fraction for all sources based on Shrivastava et al. (2011), May et al. (2013a, c), and % distribution of NEI emissions
-2	0.04	0.14	0.2	0.1754
-1	0.02	0.13	0.0	0.0141
0	0.03	0.15	0.1	0.0961
1	0.05	0.26	0.1	0.1084
2	0.07	0.15	0.2	0.1799
3	0.11	0.03	0.1	0.0949
4	0.16	0.02	0.3	0.258
5	0.20	0.01	0.0	0.0249
6	0.32	0.11	0.0	0.0483

Table 4. Configurations for OA and aerosol activation sensitivity simulations. All simulations except for CB05-SORG-DH contain the VBS treatments for OA.

Name	Gas-Phase	ΔH_{vap}	VBS	FF	POA emissions	Aerosol activation	Cumulus Scheme
CB05-SORG-DH	CB05	30 kJ mol ⁻¹	-	-	Original NEI	ARG00	Grell-Freitas
CB05-VBS-DH	CB05	30 kJ mol ⁻¹	SOA	-	Original NEI	ARG00	Grell-Freitas
CB05-POA-DH	CB05	30 kJ mol ⁻¹	SOA/POA	-	1.5×	ARG00	Grell-Freitas
CB05-POA	CB05	Epstein et al. (2010)	SOA/POA	-	1.5×	ARG00	Grell-Freitas
CB05-50%FF	CB05	Epstein et al. (2010)	SOA/POA	50%	1.5×	ARG00	Grell-Freitas
CB05-10%FF	CB05	Epstein et al. (2010)	SOA/POA	10%	1.5×	ARG00	Grell-Freitas
CB05-25%FF	CB05	Epstein et al. (2010)	SOA/POA	25%	1.5×	ARG00	Grell-Freitas
CB05-25%FF-EM3	CB05	Epstein et al. (2010)	SOA/POA	25%	3.0×	ARG00	Grell-Freitas
CB6-25%FF-EM3	CB6	Epstein et al. (2010)	SOA/POA	25%	3.0×	ARG00	Grell-Freitas
SAPRC07-25%FF-EM3	SAPRC07	Epstein et al. (2010)	SOA/POA	25%	3.0×	ARG00	Grell-Freitas
CB05-25%FF-EM3 (FN05)	CB05	Epstein et al. (2010)	SOA/POA	25%	3.0×	FN05	MSKF
CB05-25%FF-EM3 (FN05/BA10)	CB05	Epstein et al. (2010)	SOA/POA	25%	3.0×	FN05/BA10	MSKF
CB05-25%FF-EM3 (MN14)	CB05	Epstein et al. (2010)	SOA/POA	25%	3.0×	MN14	MSKF

The suffix “DH” in the case names refer to cases with the default ΔH_{vap} of 30 kJ mol⁻¹, otherwise with the semi-empirical correlation by Epstein et al. (2010). The simulations without the suffix “POA” or “FF” indicate cases with nonvolatile default POA emissions. The suffix “POA” in the case names refer to cases with semivolatile POA. The suffix “FF” in the case names refer to cases with semivolatile POA and with fragmentation and functionalization treatments, and the suffix “EM3” in the case names refer to cases with 3 times the original NEI POA emissions to take into account for missing S/IVOC species. “-” indicates not applicable.

Table 5. Range of statistics for OA/OC ratios of 1.4 and 2.1 (1.4/ 2.1) for May to June 2010. All simulations use the ARG00 aerosol activation scheme and the Grell-Freitas cumulus parameterization.

Case	Mean Obs	Mean Sim	Corr	NMB (%)	NME (%)
OC against IMPROVE					
CB05-SORG-DH	0.88	0.28/ 0.19	0.26	-68.1/ -78.7	73.9/ 80.9
CB05-VBS-DH	0.88	1.19/ 0.79	0.51	34.9/ -10.1	75.5/ 52.3
CB05-POA-DH	0.88	0.89/ 0.59	0.51	1.1/ -32.6	52.4/ 59.0
CB05-POA	0.88	1.05/ 0.70	0.51	18.9/ -20.7	63.2/ 49.2
CB05-10%FF	0.88	1.05/ 0.70	0.51	19.4/ -20.4	63.0/ 49.1
CB05-25%FF	0.88	0.86/ 0.57	0.49	-2.9/ -35.2	54.6/ 51.4
CB05-50%FF	0.88	0.56/ 0.37	0.45	-36.4/ -57.6	54.4/ 62.6
CB05-25%FF-EM3	0.88	1.09/ 0.73	0.47	23.8/ -17.5	65.9/ 50.2
CB6-25%FF-EM3	0.88	1.06/ 0.71	0.48	20.5/ -19.6	49.4/ 63.7
SAPRC07-25%FF-EM3	0.88	1.00/ 0.67	0.46	13.3/ -24.4	60.1/ 50.4
TC against IMPROVE					
CB05-SORG-DH	1.03	0.44/ 0.34	0.30	-57.6/ -66.7	67.9/ 72.3
CB05-VBS-DH	1.03	1.34/ 0.94	0.52	30.6/ -8.0	70.3/ 51.1
CB05-POA-DH	1.03	1.13/ 0.83	0.52	10.2/ -18.7	58.5/ 48.7
CB05-POA	1.03	1.29/ 0.94	0.53	25.6/ -8.5	63.8/ 48.3
CB05-10%FF	1.03	1.29/ 0.94	0.53	25.9/ -8.2	63.8/ 48.2
CB05-25%FF	1.03	1.09/ 0.83	0.51	6.8/ -21.6	55.2/ 48.2
CB05-50%FF	1.03	0.80/ 0.61	0.47	-22.0/ -40.2	50.8/ 53.4
CB05-25%FF-EM3	1.03	1.32/ 0.97	0.49	29.7/ -5.7	50.7/ 66.9
CB6-25%FF-EM3	1.03	1.30/ 0.95	0.50	27.2/ -7.3	65.2/ 50.0
SAPRC07-25%FF-EM3	1.03	1.23/ 0.90	0.48	20.6/ -11.9	61.4/ 49.4
TC against STN					
CB05-SORG-DH	2.71	1.34/ 1.10	0.29	-50.6/ -59.4	60.1/ 64.9
CB05-VBS-DH	2.71	3.35/ 2.44	0.47	23.7/ -5.8	53.1/ 42.0
CB05-POA-DH	2.71	2.88/ 2.19	0.47	6.2/ -19.0	45.5/ 41.6
CB05-POA	2.71	3.03/ 2.30	0.46	11.7/ -15.3	44.6/ 39.9
CB05-10%FF	2.71	3.03/ 2.30	0.46	11.8/ -15.3	44.5/ 39.8
CB05-25%-FF	2.71	2.66/ 2.05	0.44	-1.8/ -24.3	41.5/ 42.0
CB05-50%-FF	2.71	2.07/ 1.65	0.39	-23.8/ -39.1	43.9/ 49.4
CB05-25%FF-EM3	2.71	3.27/ 2.45	0.41	20.5/ -9.5	49.7/ 41.7
CB6-25%FF-EM3	2.71	3.39/ 2.45	0.34	24.9/ -6.4	54.8/ 45.5
SAPRC07-25%FF-EM3	2.71	3.00/ 2.28	0.41	10.7/ -16.1	45.2/ 42.0

Table 6. Statistics for evaluation at Bakersfield and Pasadena sites. A bar chart of daily average obs
 vs-versus sim values can be found in Figure 4.

Case	Mean Obs	Mean Sim	Corr	NMB (%)	NME (%)
Bakersfield					
CB05-SORG-DH	0.51	5.9e-04	-0.15	-100	100%
CB05-VBS-DH	0.51	0.67	0.41	32.5	62.0
CB05-25%FF-EM3	0.51	0.24	-0.01	-52.0	61.0
CB6-25%FF-EM3	0.51	0.28	-0.04	-45.8	59.0
SAPRC07-25%FF-EM3	0.51	0.24	-0.16	-53.1	63.0
Pasadena					
CB05-SORG-DH	0.63	0.04	-0.07	-94.0	94.0
CB05-VBS-DH	0.63	0.54	0.09	-14.5	64.3
CB05-25%FF-EM3	0.63	0.54	-0.2	-14.4	66.2
CB6-25%FF-EM3	0.63	0.62	-0.2	-2.1	70.0
SAPRC07-25%FF-EM3	0.63	0.62	0.03	-1.4	70.5

Table 7. Statistics for max 1-h and max 8-h O₃ for simulations with different gas-phases against CASTNET and AQS for May to June 2010.

CASTNET Max 1-h O₃					
Case	Mean Obs	Mean Sim	Corr	NMB (%)	NME (%)
CB05-25%FF-EM3	51.8	43.3	0.54	-16.3	21.9
CB6-25%FF-EM3	51.8	41.9	0.52	-19.1	24.1
SAPRC07-25%FF-EM3	51.8	48.3	0.51	-6.7	21.1
CASTNET Max 8-h O₃					
Case	Mean Obs	Mean Sim	Corr	NMB (%)	NME (%)
CB05-25%FF-EM3	47.4	43.0	0.54	-9.3	18.9
CB6-25%FF-EM3	47.4	41.8	0.53	-11.8	20.6
SAPRC07-25%FF-EM3	47.4	47.9	0.50	1.0	19.8
AQS Max 1-h O₃					
Case	Mean Obs	Mean Sim	Corr	NMB (%)	NME (%)
CB05-25%FF-EM3	51.0	49.9	0.55	-2.1	18.2
CB6-25%FF-EM3	51.0	51.5	0.43	1.0	20.8
SAPRC07-25%FF-EM3	51.0	59.3	0.44	16.4	26.1
AQS Max 8-h O₃					
Case	Mean Obs	Mean Sim	Corr	NMB (%)	NME (%)
CB05-25%FF-EM3	46.2	46.0	0.54	-0.4	18.6
CB6-25%FF-EM3	46.2	47.4	0.47	2.6	20.3
SAPRC07-25%FF-EM3	46.2	53.7	0.46	16.3	25.4
IMPROVE PM_{2.5}					
Case	Mean Obs	Mean Sim	Corr	NMB (%)	NME (%)
CB05-25%FF-EM3	4.9	3.8	0.64	-22.0	40.6
CB6-25%FF-EM3	4.9	4.1	0.65	-16.5	39.6
SAPRC07-25%FF-EM3	4.9	3.5	0.60	-28.5	42.9
STN PM_{2.5}					
Case	Mean Obs	Mean Sim	Corr	NMB (%)	NME (%)
CB05-25%FF-EM3	11.1	8.8	0.48	-20.6	40.7
CB6-25%FF-EM3	11.1	10.0	0.37	-9.3	44.3
SAPRC07-25%FF-EM3	11.1	7.7	0.40	-30.5	45.2
AQS PM₁₀					
Case	Mean Obs	Mean Sim	Corr	NMB (%)	NME (%)
CB05-25%FF-EM3	24.6	7.3	0.08	-70.2	73.5
CB6-25%FF-EM3	24.6	8.0	0.09	-67.7	71.8
SAPRC07-25%FF-EM3	24.6	6.9	0.09	-71.9	74.8

Table 8. Statistics for model evaluation for simulated CDNC against MODIS-derived CDNC from Bennartz (2007). All cases use the Grell-Freitas cumulus parameterization.

Case	Mean Obs	Mean Sim	Corr	NMB (%)	NME (%)
CB05-SORG-DH	162.1	96.0	0.28	-40.8	50.4
CB05-VBS-DH	162.1	106.0	0.28	-34.6	50.6
CB05-POA-DH	162.1	115.0	0.29	-29.1	47.4
CB05-POA	162.1	117.3	0.29	-27.7	47.3
CB05-10%FF	162.1	117.1	0.29	-27.8	47.2
CB05-25%-FF	162.1	116.4	0.29	-28.2	47.3
CB05-50%-FF	162.1	114.7	0.29	-29.2	47.4
CB05-25%FF-EM3	162.1	116.2	0.29	-28.3	47.3
CB6-25%FF-EM3	162.1	110.4	0.30	-31.9	47.3
SAPRC07-25%FF-EM3	162.1	77.3	0.26	-52.3	55.8

Table 9. Statistics for simulated CDNC for CB05-25%FF-EM3 against MODIS-derived CDNC from Bennartz (2007) for May to June 2010. All cases use the MSKF cumulus parameterization.

Case	Mean Obs	Mean Sim	Corr	NMB (%)	NME (%)
ARG00	162.1	104.8	0.31	-35.4	49.9
FN05	162.1	173.8	0.26	7.1	93.0
FN05/BA10	162.1	160.8	0.27	-0.8	87.9
MN14	162.1	168.9	0.27	4.2	89.6

Figures

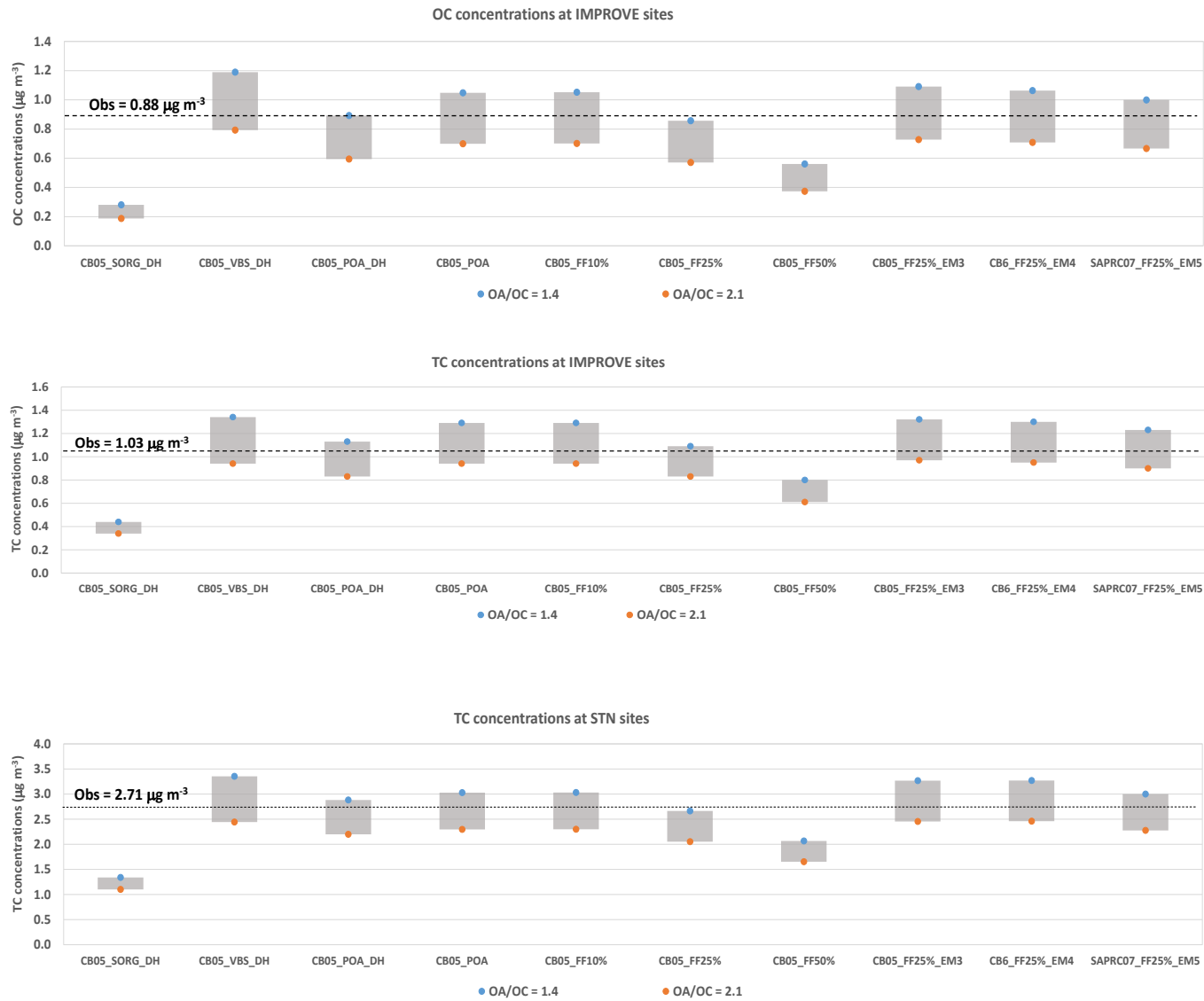
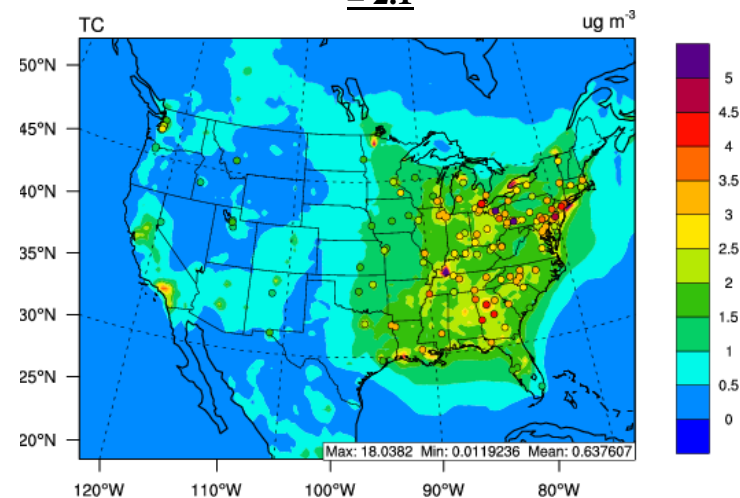


Figure 1. Sim OC and TC concentrations against observations from IMPROVE and STN under two OA/OC ratios: 1.4 and 2.1, resulting in a range of possible OC or TC values denoted by the gray bars. The obs OC or TC is denoted by the horizontal dotted line.

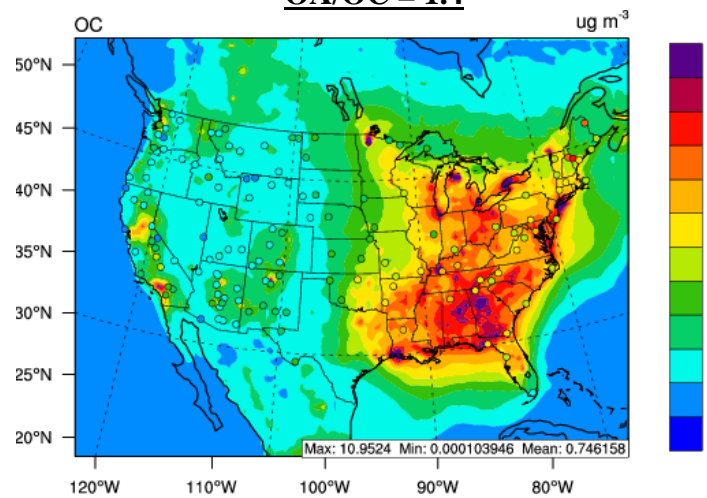
IMPROVE OC (markers) with Sim OC (background) with OA/OC = 2.1



STN TC (markers) with Sim TC (background) with OA/OC = 2.1



IMPROVE OC (markers) with Sim OC (background) with OA/OC = 1.4



STN TC (markers) with Sim TC (background) with OA/OC = 1.4

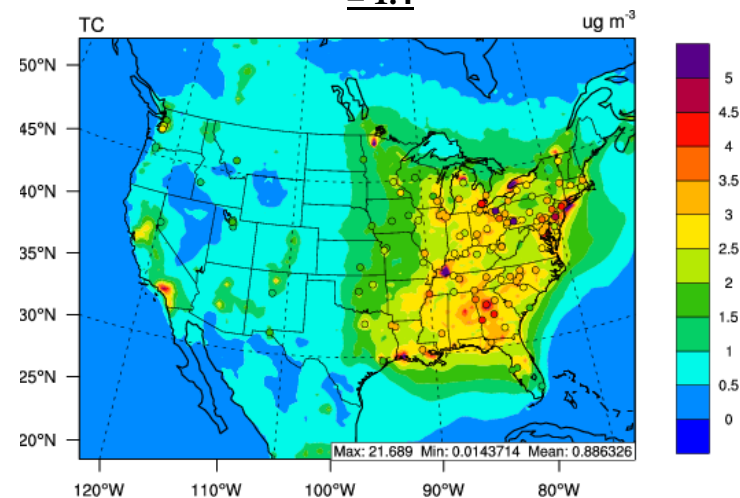


Figure 2. Overlay of obs data (markers) ~~vs.~~versus sim data (background) for IMPROVE OC and STN TC and for OA/OC ratios of 1.4 and 2.1 for the case CB05_25%FF_EM3.

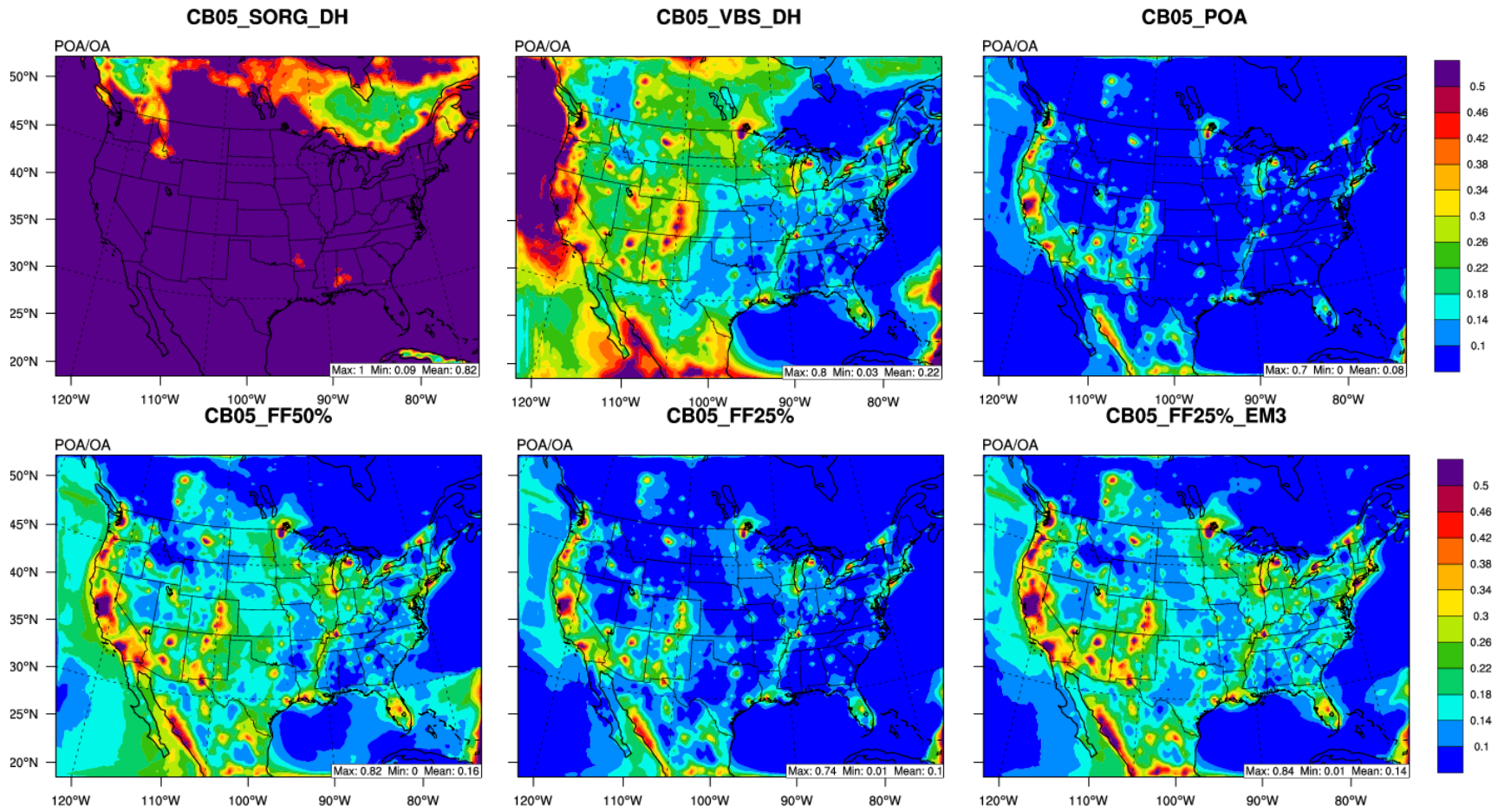


Figure 3. POA/OA ratios of sim data from various sensitivity simulation cases.

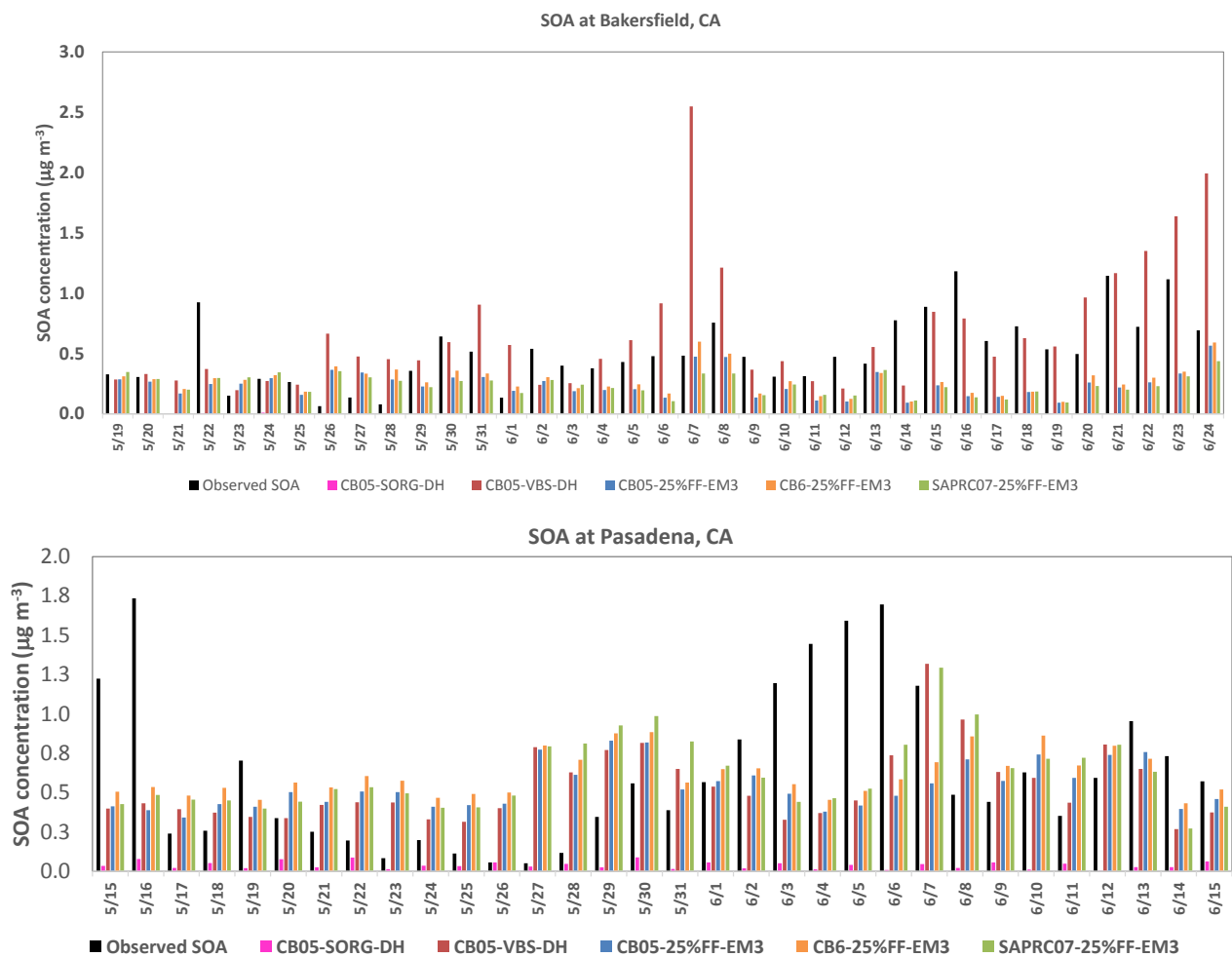


Figure 4. Comparison of obs SOA ~~vs.~~ versus sim SOA at CalNex sites in Bakersfield and Pasadena in California.

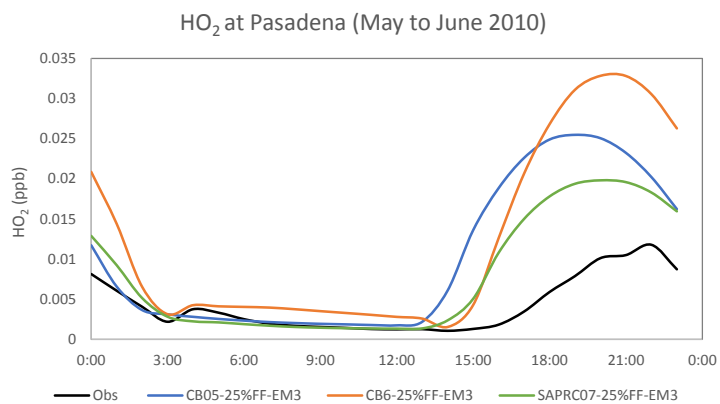
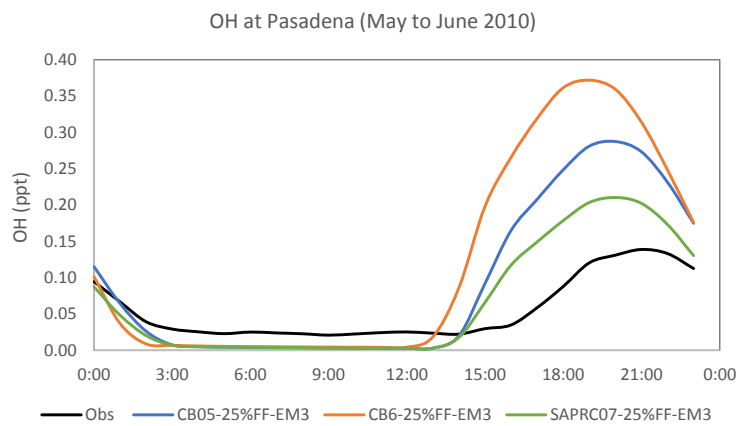
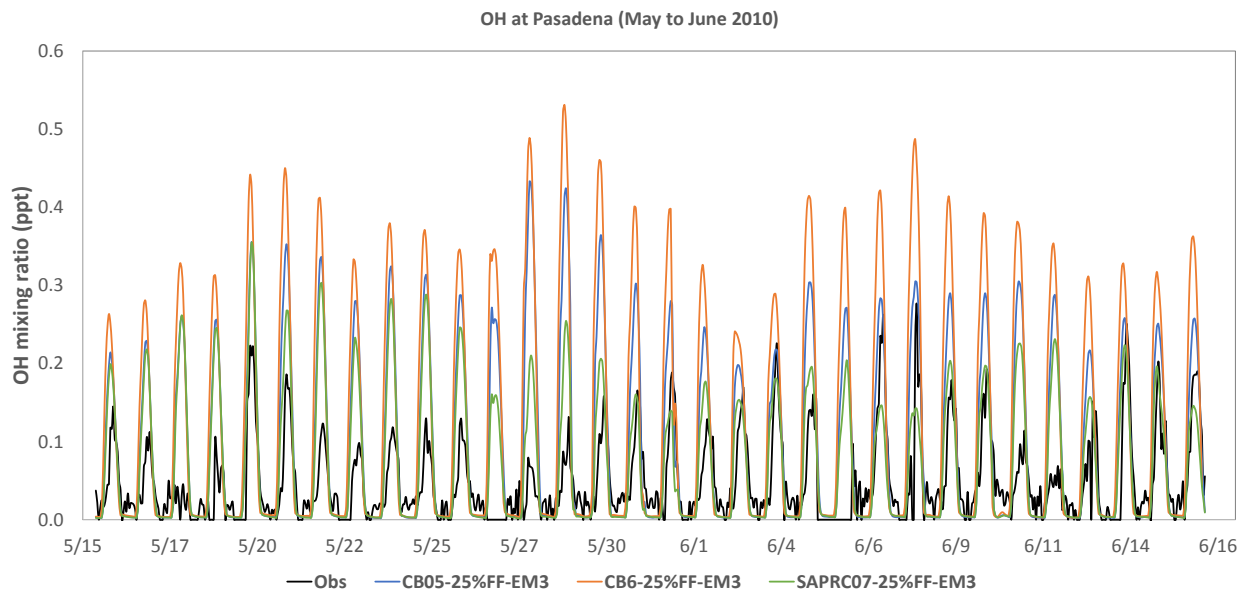


Figure 5. Time series of OH and diurnal plots of OH and HO₂ at Pasadena, CA during CALNEX, 2010.

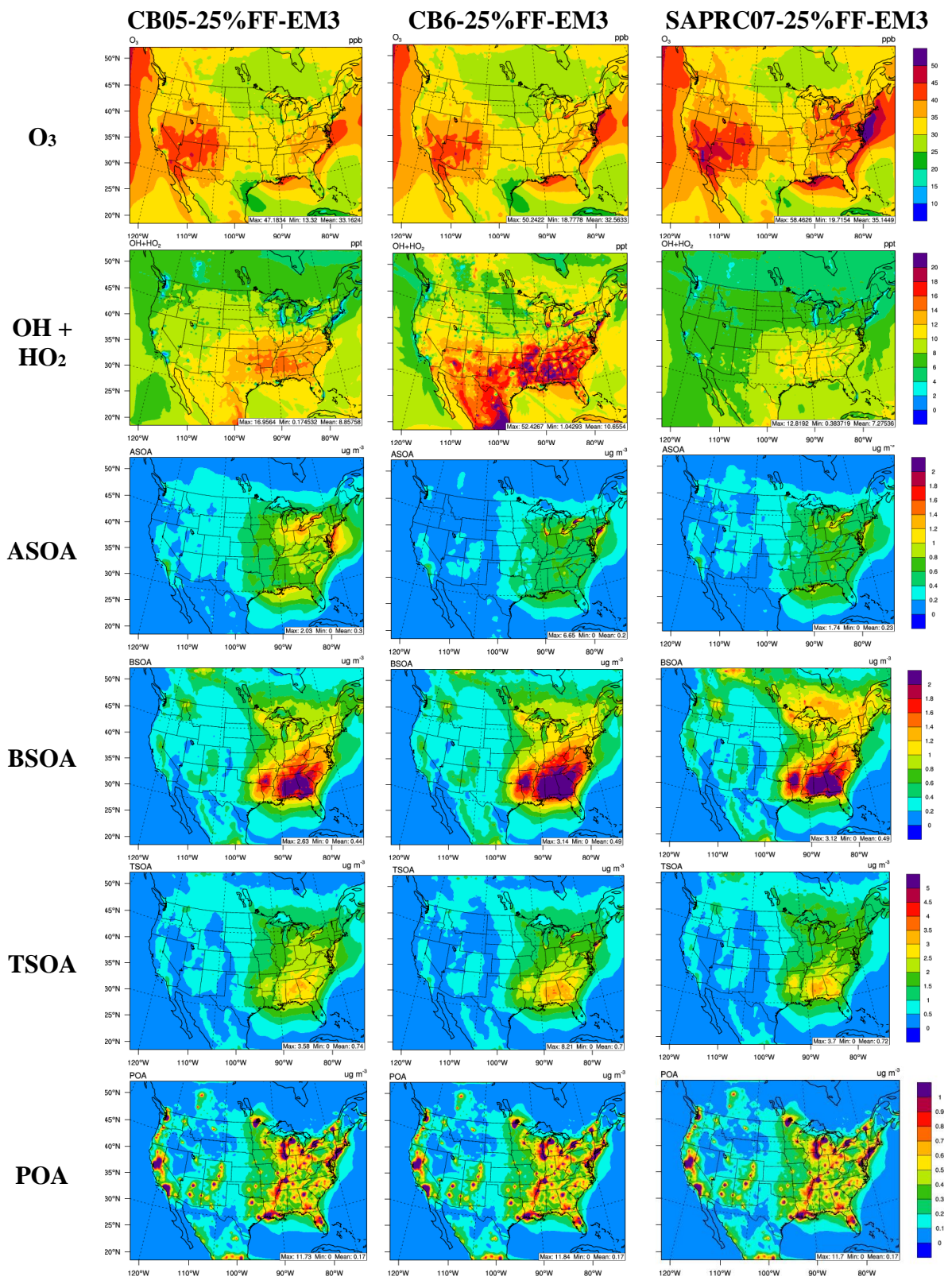


Figure 6. Spatial plots of several gas and aerosol species for the three cases with different gas-phase mechanisms.

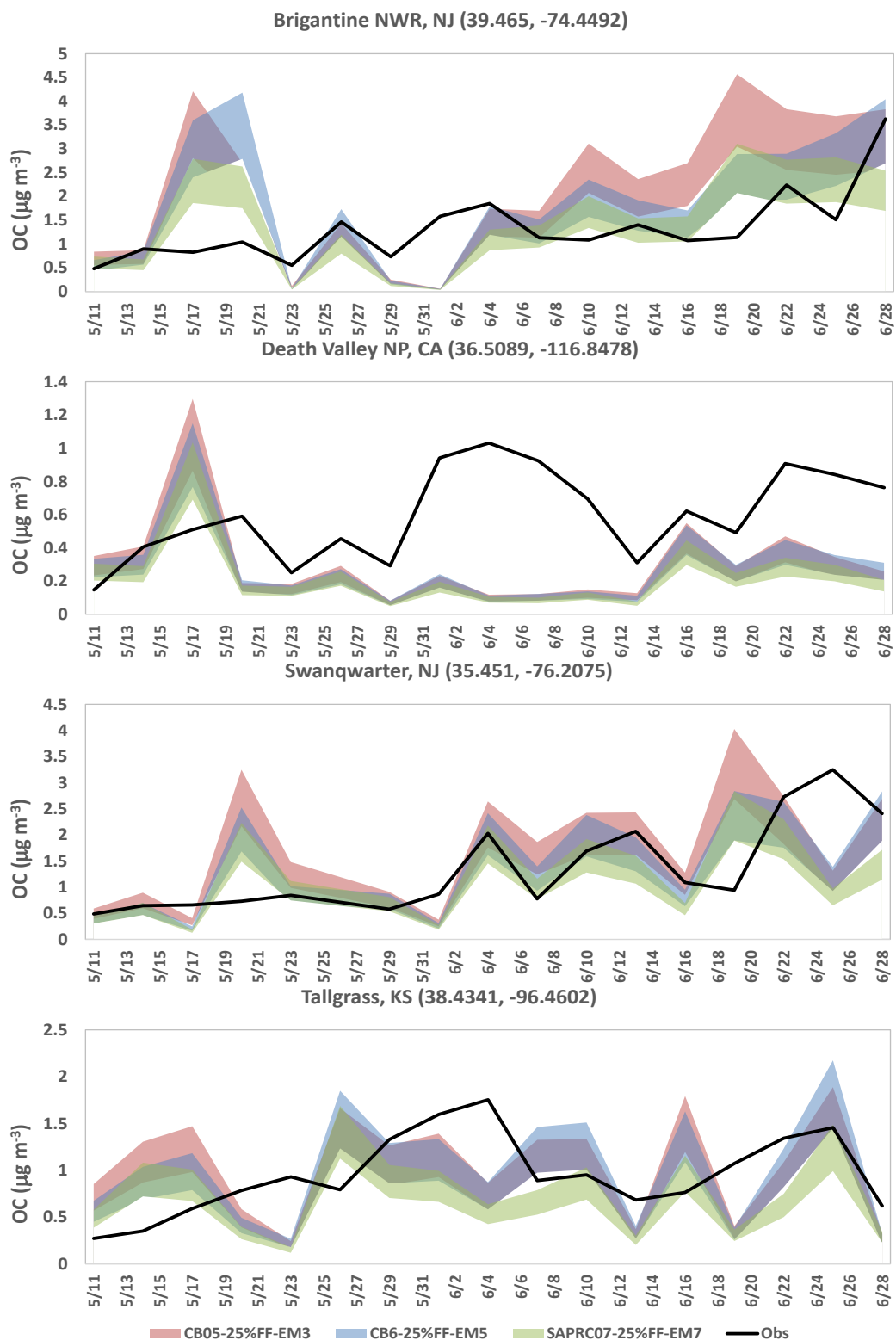


Figure 7. Timeseries plots of IMPROVE OC *vs. versus* simulated OC at selected sites from sensitivity simulations of different gas-phase mechanisms. The colored bands represent the range of OC values for ratios 1.4 to 2.1.

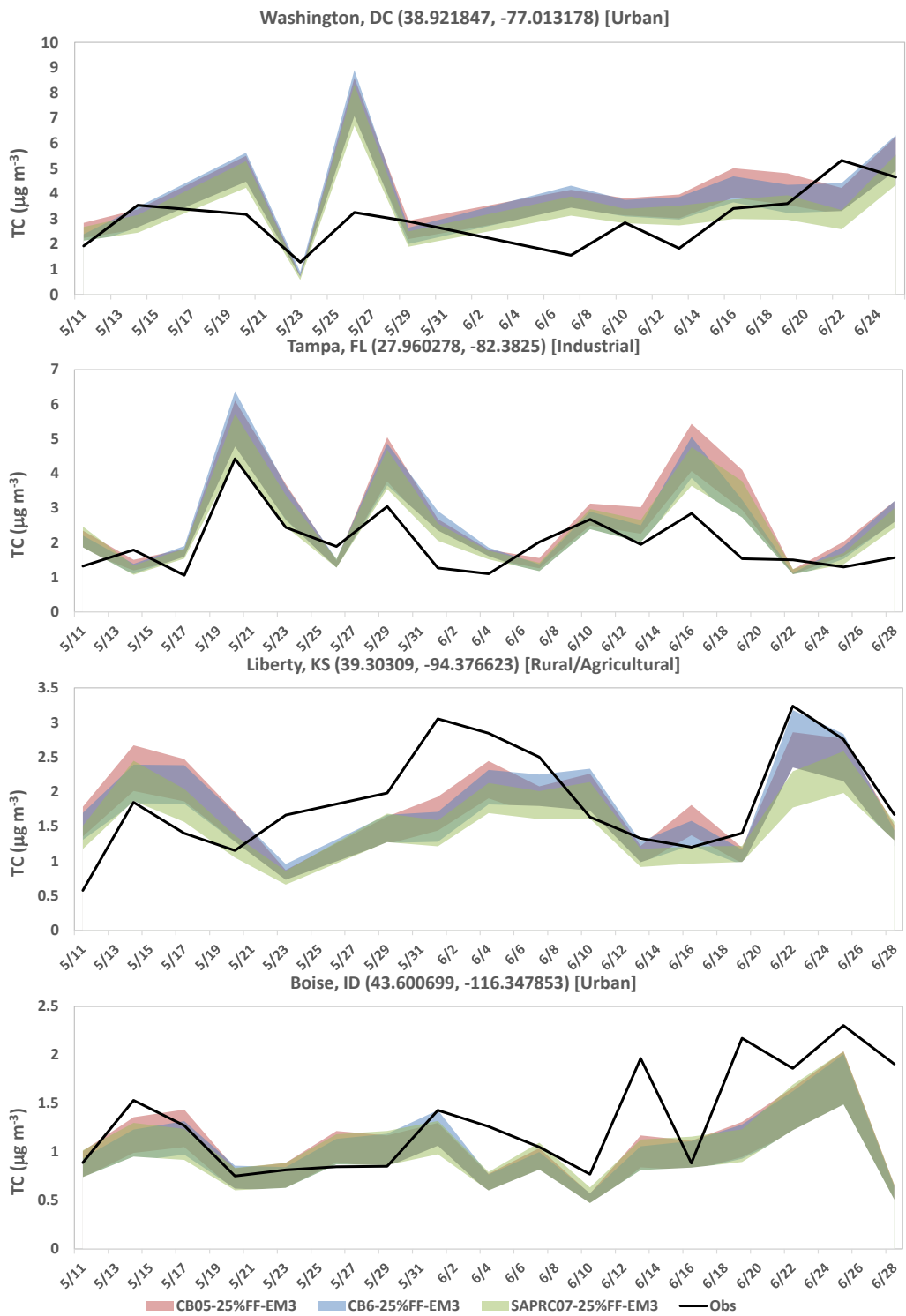


Figure 8. Timeseries plots of STN TC vs-versus simulated TC at selected sites from sensitivity simulations of different gas-phase mechanisms. The colored bands represent the range of OC values for ratios 1.4 to 2.1.

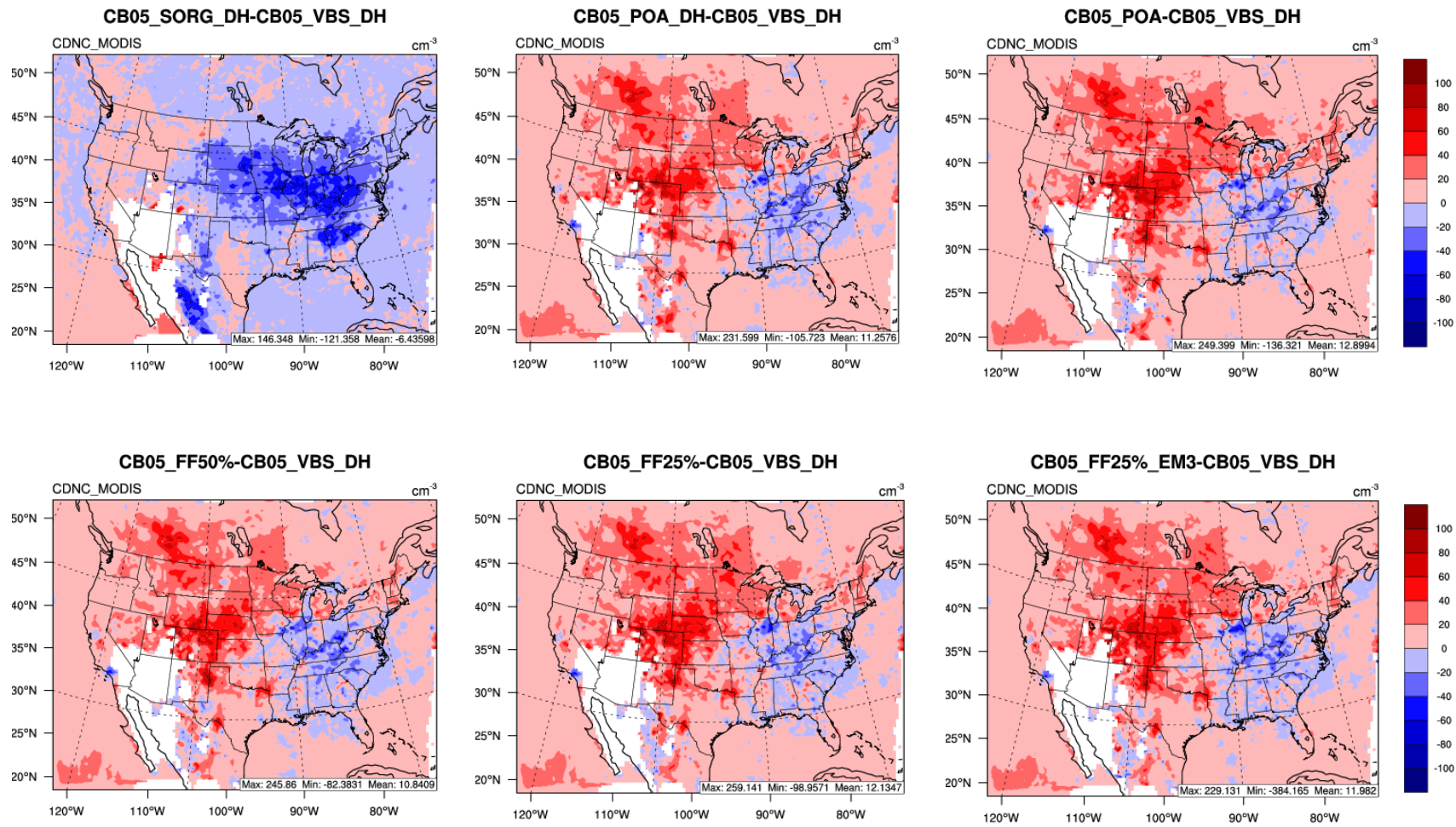


Figure 9. Impact of different VBS cases on CDNC in warm clouds. The plots show the differences between the different sensitivity simulations and CB05_VBS-DH.

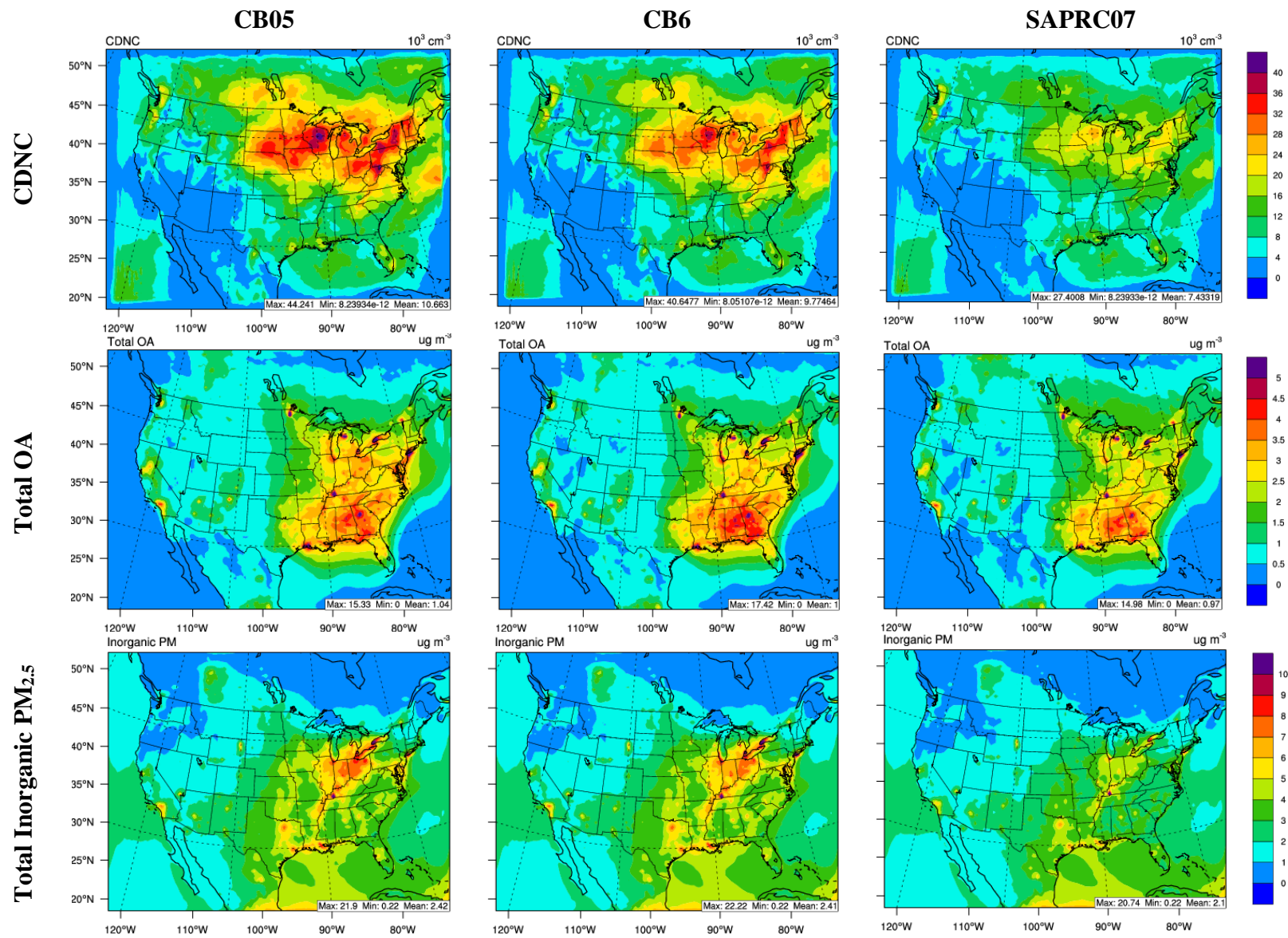


Figure 10. Spatial plots of total column CDNC, total surface OA and total inorganic PM_{2.5} concentrations from simulations with different gas-phase mechanisms.

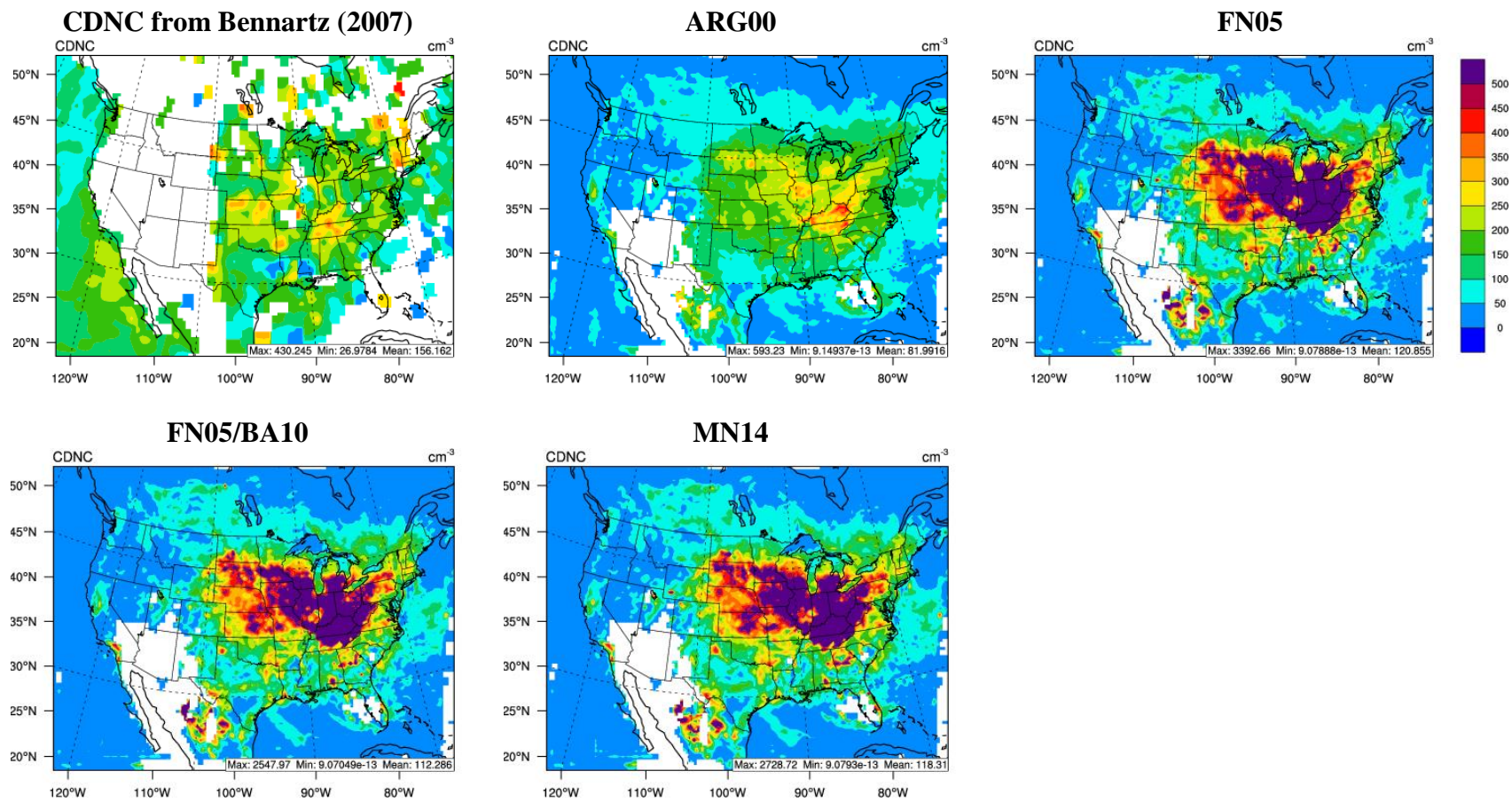


Figure 11. Spatial plots for MODIS-derived CDNC from Bennartz (2007) and simulated in-cloud column CDNC from CB05_25%FF_EM3 ARG00, FN series, and MN14 from May to June 2010.

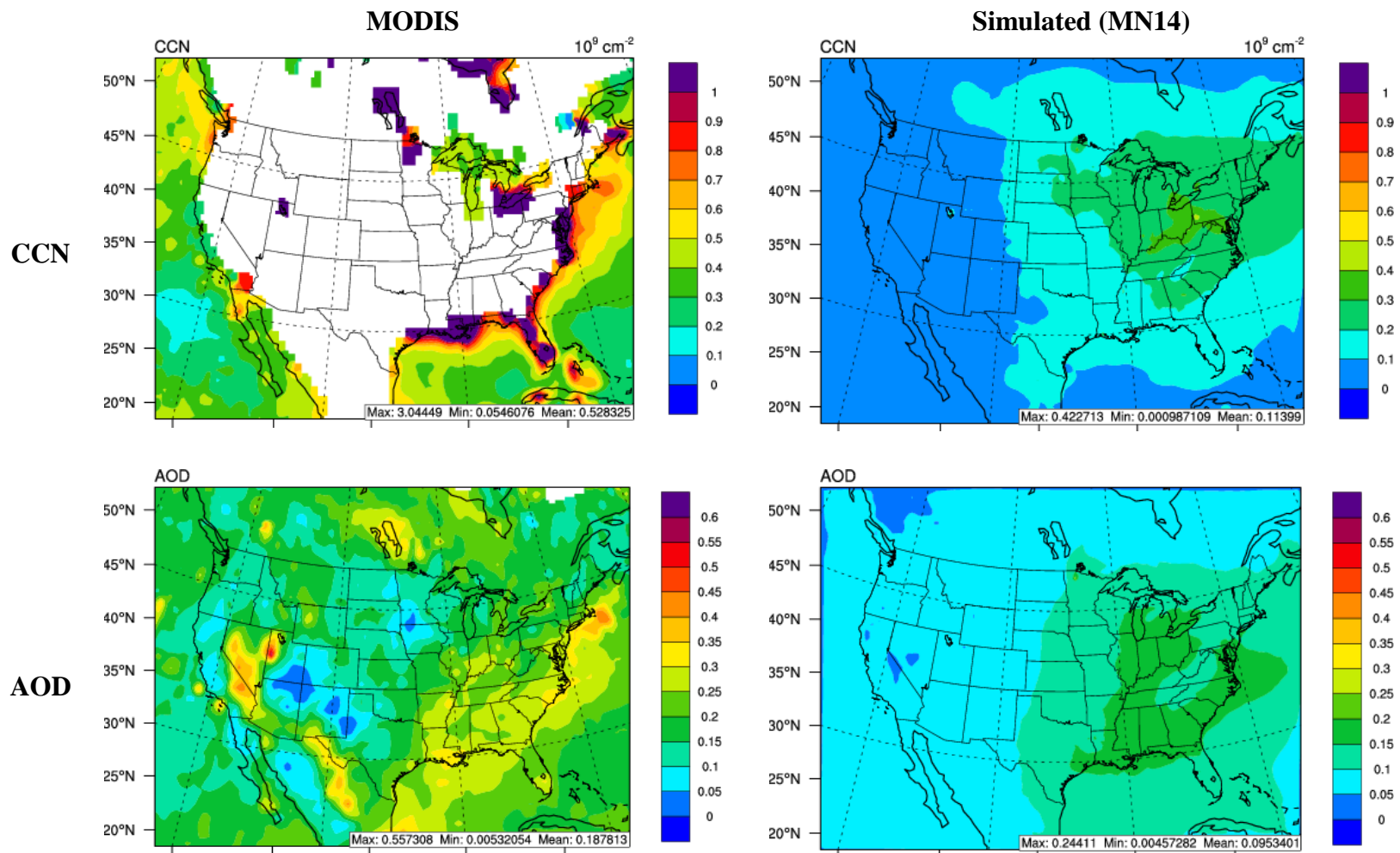


Figure 12. Spatial plots of MODIS CCN and AOD against simulated CCN and AOD from MN14 with CB05_25%FF_EM3.