1 Secondary organic aerosol enhanced by increasing atmospheric oxidizing capacity in

2 Beijing-Tianjin-Hebei (BTH), China

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20 **Abstract**. The implementation of the Air Pollution Prevention and Control Action Plan in

21 China since 2013 has profoundly altered the ambient pollutants in the Beijing-Tianjin-Hebei

22 region (BTH). Here we show observations of substantially increased O_3 concentrations

23 (about 30%) and a remarkable increase in the ratio of organic carbon (OC) to elemental

24 carbon (EC) in BTH during the autumn from 2013 to 2015, revealing an enhancement in

25 atmospheric oxidizing capacity (AOC) and secondary organic aerosol (SOA) formation. To

26 explore the impacts of increasing AOC on the SOA formation, a severe air pollution episode

27 from 3 to 8 October 2015 with high O_3 and $PM_{2.5}$ concentrations is simulated using the

28 WRF-Chem model. The model performs reasonably well in simulating the spatial

29 distributions of $PM_{2.5}$ and O_3 concentrations over BTH and the temporal variations of $PM_{2.5}$,

30 O_3, NO_2, OC, and EC concentrations in Beijing compared to measurements. Sensitivity

31 studies show that the change in AOC substantially influences the SOA formation in BTH. A

32 sensitivity case characterized by a 31% O_3 decrease (or 36% OH decrease) reduces the SOA

33 level by about 30% and the SOA fraction in total organic aerosol by 17% (from 0.52 to 0.43,

34 dimensionless). Spatially, the SOA decrease caused by reduced AOC is ubiquitous in BTH,

35 but the spatial relationship between SOA concentrations and the AOC is dependent on the

36 SOA precursor distribution. Studies on SOA formation pathways further show that, when the

37 AOC is reduced, the SOA from oxidation and partitioning of semi-volatile POA and

38 co-emitted intermediate volatile organic compounds (IVOCs) decreases remarkably, followed

39 by those from anthropogenic and biogenic VOCs. Meanwhile, the SOA decrease in the

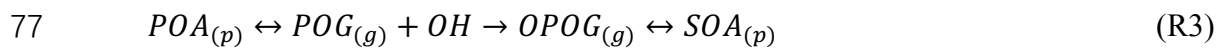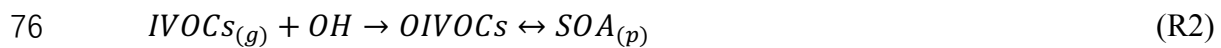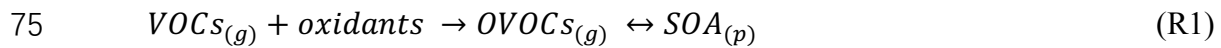40 irreversible uptake of glyoxal and methylglyoxal on aerosol surfaces is negligible.

1 Introduction

Severe haze pollutions characterized by exceedingly high concentrations of fine particulate matter ($PM_{2.5}$) in Beijing-Tianjin-Hebei (BTH), China have drawn much attention from the public, government, and science community (Han et al., 2014; Jiang et al., 2015; Li et al., 2017a; Quan et al., 2014; Wang et al., 2016a). Elevated levels of $PM_{2.5}$ concentrations not only deteriorate air quality and visibility (Cao et al., 2012a; Feng et al., 2016; Seinfeld and Pandis, 2006), but also threat the public health and ecosystem (Cao et al., 2012b; Tie et al., 2016). In addition, $PM_{2.5}$ also modulates the energy budget of the earth system directly through absorbing and scattering the incident solar radiation and indirectly via acting as cloud condensation nuclei (CCN) and ice nuclei (IN) and subsequently altering cloud albedo and lifetime (Li et al., 2008; 2009; Wang et al., 2013; 2016b; 2018; Zhou et al., 2017).

Organic aerosol (OA) is a key component of $PM_{2.5}$ in ambient air, constituting of 20~90% of the $PM_{2.5}$ mass concentration (Kanakidou et al., 2005; Zhang et al., 2007). Previous studies have confirmed a large mass fraction of OA in ambient $PM_{2.5}$ in various Chinese cities. For example, Huang et al. (2014) have reported that OA accounts for 30~50% of the total $PM_{2.5}$ mass in megacities in China (e.g., Beijing, Shanghai, Guangzhou, and Xi'an) during severe haze episodes. Positive matrix factorization (PMF) analyses of the aerosol chemical speciation monitor (ACSM) measurements in Beijing have shown that OA contributes 40% and 52% of refractory submicron particulate matters in summer 2011 and winter 2012, respectively (Sun et al., 2013; 2012). Over BTH, Huang et al. (2017) have demonstrated that OA constitutes the most important part in the major chemical components of gravimetric $PM_{2.5}$ (20~25%) based on measurements at 3 urban sites from June 2014 to April 2015.

OA is traditionally categorized into primary and secondary organic aerosols (referred to as POA and SOA, respectively) in terms of its source and formation in the atmosphere. POA is the OA directly emitted into the atmosphere, and SOA is formed through a series of

chemical conversions of precursors and gas-particle partitioning, closely associated with the

abundance of oxidants in the atmosphere and ambient temperature (Feng et al., 2016; Li et al.,

2011b; Tsimpidi et al., 2010). SOA precursors mainly include volatile organic compounds

(VOCs) emitted from anthropogenic and biogenic sources (Odum et al., 1996; Pankow, 1994),

primary organic gases (POG) emitted or formed in the evaporation of POA, and intermediate

VOCs (IVOCs) co-emitted with the POA (Lipsky and Robinson, 2006; Robinson et al., 2007;

Shrivastava et al., 2006). The pathway of SOA formation is illustrated as follows (Li et al.,

2011b; Robinson et al., 2007):

$$VOCs_{(g)} + oxidants \rightarrow OVOCs_{(g)} \leftrightarrow SOA_{(p)} \tag{R1}$$

$$IVOCs_{(g)} + OH \rightarrow OIVOCs \leftrightarrow SOA_{(p)} \tag{R2}$$

$$POA_{(p)} \leftrightarrow POG_{(g)} + OH \rightarrow OPOG_{(g)} \leftrightarrow SOA_{(p)} \tag{R3}$$

where the subscript g and p denote gas- and particle-phase, respectively. OVOCs, OIVOCs,

and OPOG are oxidized VOCs, IVOCs, and POG, respectively. The oxidants in the chemical

reactions mainly include ozone (O_3), hydroxyl radical (OH) and nitrate radical (NO_3).

Apparently, the abundance of oxidants in the atmosphere plays an important role in the SOA

formation, and increasing oxidants potentially enhance SOA formation. It is worth noting that

heterogeneous reactions also play a considerable role in SOA formation (Fu et al., 2009; Li et

al., 2011b).

Over the last decade, O_3 concentrations have dramatically increased in eastern China. For

example, Cheng et al. (2016) have reported an increasing trend of the daily maximum 1h O_3

concentration over Beijing from 2004 to 2015. Ma et al. (2016) have observed a significant

increase of surface O_3 concentrations at a rural station in the north of eastern China from

2003 to 2015. Since 2013, the implementation of the Air Pollution Prevention and Control

Action Plan (APPCAP) in China have profoundly altered the air pollutants in BTH (He et al.,

2017; Li et al., 2017b; Wu et al., 2017). He et al. (2017) have reported that the ambient OA

92 concentration has been significantly reduced by 27.5%, 17.4%, and 14.0% in Beijing, Tianjin,

93 and Hebei, respectively, from 2013 to 2017. The increasing O_3 concentration has become a

94 new culprit for the deterioration of the air quality in eastern China (Li et al., 2017b; Wu et al.,

95 2017). Li et al. (2017b) have reported that the O_3 concentration has increased by 10% from

96 2013 to 2015 averaged over 65 cities of eastern China during April ~ September. In Beijing,

97 the summertime O_3 concentration has increased by 23% from 2013 to 2015 (Wu et al., 2017).

98 Such an increasing trend of O_3 concentrations reflects an enhancement of the atmospheric

99 oxidizing capacity (AOC), which, as expected, potentially influences the SOA formation and

100 OA components. Therefore, it is imperative to evaluate the impact of the increasing AOC on

101 the SOA formation over BTH.

102 The objective of this study is to evaluate the impact of the increasing AOC on OA

103 components in BTH (Figure 1) during a haze episode in the autumn of 2015 using the

104 WRF-Chem model. Model and configuration are described in Sect. 2; the results and

105 discussion are presented in Sect. 3. The conclusions are drawn in Sect. 4.

106

107 **2   Model and method**

108 **2.1 WRF-Chem model and configuration**

109 In this study, simulations are performed using a specific version of the WRF-Chem

110 model (Grell et al., 2005) developed by Li et al. (2011b; 2011a; 2012; 2010). The model

111 includes a flexible gas phase chemical module and the Models-3 community multiscale air

112 quality (CMAQ) aerosol module (Binkowski and Roselle, 2003). The photolysis rates are

113 calculated using the FTUV module (Li et al., 2005; Tie et al., 2003) which takes into account

114 the effects of clouds and aerosols on photochemistry. A non-traditional SOA module based on

115 the volatility basis-set (VBS) method (Donahue et al., 2006; Robinson et al., 2007) is

116 incorporated into the model to simulate organic aerosols. In this module, POA is distributed

117   in logarithmically spaced volatility bins and presumed to be semi-volatile and

118   photochemically reactive (Li et al., 2011b). The module uses 9 surrogate species with

119   saturation concentration ranging from 10^{-2} to 10^{6} $\mu g\ m^{-3}$ at room temperature to represent

120   POA compositions (Shrivastava et al., 2008). IVOCs, co-emitted with the POA but in the gas

121   phase, are also oxidized by OH to form SOA. In addition, the SOA formation from glyoxal

122   and methylglyoxal is included in the module, which is parameterized as a first-order

123   irreversible uptake on aerosol surface with a reactive uptake coefficient of 3.7×10^{-3}

124   (Volkamer et al., 2007; Zhao et al., 2006). Inorganic aerosols are calculated by the

125   ISORROPIA version 1.7 (Nenes et al., 1998). The GOCART (Georgia Tech/Goddard Global

126   Ozone Chemistry Aerosol Radiation and Transport model) dust module is used to estimate

127   the emission, transport, dry deposition, and gravitational settling of dust (Ginoux et al., 2001).

128   The biomass burning emissions are from the Fire Inventory from NCAR (FINN)

129   (Wiedinmyer et al., 2011; 2006). The dry deposition of chemical species is parameterized

130   following Wesely (1989) and the wet deposition is calculated using the method in the CMAQ

131   module (Binkowski and Roselle, 2003). Specifically, the surface and upper air observational

132   wind fields from China Meteorological Administration (CMA) during the study period are

133   assimilated using the four-dimensional data assimilation (FDDA) method to better simulate

134   meteorological fields.

135   A severe haze episode from 3 to 8 October 2015 in BTH with high O_3 and $PM_{2.5}$

136   concentrations is simulated. The model is configured with one single domain which is

137   centered at 116°E and 38°N with grid spacing of 6 km×6 km (200×200 grid cells).

138   Thirty-five stretched vertical levels with spacing ranging from about 30 m near surface, to

139   500 m at 2.5 km, and 1 km above 14 km are used in the model configuration. The monthly

140   average anthropogenic emission inventory is developed by Zhang et al. (2009) and Li et al.

141   (2017c), with the base year of 2013, including agriculture, industry, power generation,

142 residential, and transportation sources. The temporal resolution of emissions used in

143 simulations is 1 hour, and the temporal allocation for different sources follows those in Zhang

144 et al. (2009). Figure 2 presents the spatial distributions of anthropogenic volatile organic

145 compounds (VOCs) and organic carbon (OC) emissions in October, showing high emissions

146 in urban areas. The emissions of various species in Beijing, Tianjin, Hebei, and the entire

147 domain in October 2015 are summarized in Table 1. Biogenic emissions are calculated online

148 using the MEGAN (Model of Emissions of Gases and Aerosol from Nature) model (Guenther

149 et al., 2006). The model configuration is presented in Table 2.

150 **2.2 Pollutant measurements**

151 Measurement data used in this study include the hourly concentrations of O_3, NO_2, SO_2,

152 CO, and $PM_{2.5}$ from ambient monitoring stations of China's Ministry of Environment and

153 Ecology (China MEE) and hourly OC and EC concentrations in $PM_{2.5}$ measured hourly at

154 Chinese Research Academy of Environmental Sciences (CRAES) using a Sunset OC/EC

155 Analyzer (RT-4, Sunset Lab, USA). The OC/EC analyzer has been widely used in ambient

156 and indoor OC/EC detections in China (Liu et al., 2018; Wei et al., 2014). In addition, hourly

157 submicron POA and SOA concentrations are obtained from the ACSM measurement

158 analyzed using the PMF method at National Center for Nanoscience and Technology (NCNT)

159 in Beijing.

160 **2.3 Model simulations**

161 We define the simulation with the AOC in October 2015 as the reference (REF). The

162 model result in REF is compared with the observations to evaluate the model performance.

163 To examine the impact of increasing AOC on OA components, we perform 4 sensitivity

164 experiments (SEN1~4) by varying AOC. Compared with the REF simulation, we decrease all

165 the photolysis frequencies by 10%, 20%, 30%, and 40%, respectively, in the model

166 simulations.

167   **2.4 Statistic method**

168   The mean bias (MB), normalized mean bias (NMB), root mean square error (RMSE),

169   index of agreement (IOA), and linear Pearson correlation coefficient (*r*) are selected to

170   evaluate the WRF-Chem model simulations against observations.

171    $$MB = \frac{1}{N}\sum_{i=1}^{N}(P_i - O_i)$$ (1)

172    $$NMB = \frac{\sum_{i=1}^{N}(P_i - O_i)}{\sum_{i=1}^{N} O_i} \times 100\%$$ (2)

173    $$RMSE = \left[\frac{1}{N}\sum_{i=1}^{N}(P_i - O_i)^2\right]^{\frac{1}{2}}$$ (3)

174    $$IOA = 1 - \frac{\sum_{i=1}^{N}(P_i - O_i)^2}{\sum_{i=1}^{N}(|P_i - \bar{O}| + |O_i - \bar{O}|)^2}$$ (4)

175    $$r = \frac{\sum_{i=1}^{N}(P_i - \bar{P})(O_i - \bar{O})}{\sqrt{\sum_{i=1}^{N}(P_i - \bar{P})^2}\sqrt{\sum_{i=1}^{N}(O_i - \bar{O})^2}}$$ (5)

176   where P_i and O_i are the simulated and observed variables, respectively. N is the total

177   number of predictions. $\bar{P}$ and $\bar{O}$ denote the average of predictions and observations,

178   respectively. IOA ranges from 0 to 1 theoretically, with 1 suggesting perfect agreement

179   between predictions and observations.

180

181**2** **3   Results and discussion**

182   **3.1 Observed increasing O₃ concentration and OC/EC ratio**

183   Figure 3a shows the annual variation of measured mean concentrations of O_3, NO_2, SO_2,

184   CO, and $PM_{2.5}$ over BTH in the autumn from 2013 to 2017. To better present the pollution

185   characteristics in autumn, the observations from 15 September to 14 November are selected

186   in this study, which avoids the heating period (starting from 15 November) in northern China.

187   Obvious decreasing trends in NO_2, SO_2, CO, and $PM_{2.5}$ concentrations during recent years

188   are observed since the implementation of APPCAP (Figure 3a). The O_3 concentration,

189   however, has increased by about 30% during the same period. Such an O_3 increase indicates a

190 considerable enhancement of the AOC, considering the controlling role of O_3 in the AOC in

191 the troposphere (Brasseur et al., 1999). The reason for the AOC or O_3 increase since 2013

192 still remains elusive. Li et al. (2018) have proposed that the O_3 increase in China since 2013

193 is associated with the decreased removal efficiency of HO_x (OH + peroxy) on aerosol

194 surfaces caused by the reduced aerosol concentrations since the implementation of APPCAP.

195 However, further studies need to be conducted to evaluate the O_3 contribution of the

196 photolysis change caused by the aerosol-radiation interaction and aerosol-cloud interaction

197 induced by decreasing aerosols in China.

198 As important $PM_{2.5}$ components, organic carbon (OC) and elemental carbon (EC) are

199 measured in Beijing in the autumns from 2013 to 2015 (Figure 3b). The measured OC/EC

200 ratio has substantially increased during the 3 years (about 44%). There are two possible

201 reasons for this. Firstly, the increase might be attributed, at least in part, to the increasing

202 AOC, which enhances the SOA formation. Secondly, the increase might be caused by the

203 changes in OC and EC emissions due to the implementation of APPCAP. The large

204 variability in OC and EC concentrations in Figure 3b suggests considerable emission changes,

205 although it is still difficult to evaluate exactly how much the emissions have been changed.

206 Since SOA formation is closely associated with the abundance of oxidants (Li et al., 2011b;

207 Robinson et al., 2007), OA in BTH is expected to be more oxygenated (add oxygen) and

208 hence to increase in mass with enhanced AOC.

209 **3.2 Model evaluation**

210 **3.2.1 Meteorological fields**

211 Model performance in meteorological fields is crucial for the simulation of air pollutants

212 (Bei et al., 2010; 2012; 2017). Figures 4 and 5 present the simulated temporal variations of

213 the surface temperature, relative humidity, wind speed, and wind direction against

214 observations at 4 meteorological stations (Beijing, Tianjin, Shijiazhuang, and Baoding,

215 Figure 1) in BTH.

216 The model performs well in reproducing the observed diurnal cycles of the surface

217 temperature and relative humidity at the 4 stations (Figure 4). The simulated temporal

218 variations of temperature and relative humidity are in good agreement with the observations

219 at the meteorological station in Tianjin. However, in the other 3 cities, the model generally

220 cannot well reproduce the fairly low temperature and high relative humidity during nighttime.

221 In general, the model replicates the low winds during 3-7 October in Beijing, Tianjin, and

222 Baoding, but slightly overestimates the wind speed in Shijiazhuang, particularly in the

223 morning of 8 October (Figure 5). The model fails to produce the occurrence of the strong

224 wind with a maximum speed exceeding 10 m s^{-1} and the wind direction at noon on 8 October

225 in Beijing. Overall, the model still generally captures the temporal variations of wind

226 directions in the 4 cities.

227 **3.2.2 PM$_{2.5}$, O$_3$, and NO$_2$**

228 The spatial distributions of simulated and observed daily PM$_{2.5}$ concentration during the

229 period from 3 to 8 October 2015 are presented in Figure 6 along with wind fields. This haze

230 event in BTH can be divided into 4 stages: (1) startup (3 October), (2) development (4

231 October), (3) maturation (5-7 October), and (4) dissipation (8 October). On 3 October, the

232 haze formed in Shandong and southern BTH, accompanied by weak winds near the surface

233 (< 2 m s^{-1}). On 4 October, the southerly wind prevailed, causing trans-boundary transport of

234 air pollutants from south to north, and the PM$_{2.5}$ concentration in BTH rapidly increased.

235 From 5 to 7 October, the southerly wind continued and the haze became persistently severe in

236 BTH. Finally, a strong northerly wind cleaned up the haze within several hours on 8 October.

237 The model reasonably reproduces the haze evolution in BTH, but it generally underestimates

238 the PM$_{2.5}$ concentration in Shandong province.

239 Figure 7 shows the observed and simulated spatial distribution of peak O$_3$ concentrations

at 14:00 (local time, hereafter) during the episode. Similar to $PM_{2.5}$, the high O_3 concentration first occurred in Shandong province on 3 October, and propagated to BTH on 4 October. During the maturation period, the O_3 level in BTH still remained high. The simulated spatial distributions of O_3 concentrations generally agree well with the observations during the four stages, but underestimation or overestimation still exists.

Figure 8 shows the temporal variations of the simulated and observed surface $PM_{2.5}$, O_3, and NO_2 concentrations averaged over 12 ambient monitoring stations in Beijing. The simulated and observed $PM_{2.5}$ temporal pattern clearly shows the 4 stages of the haze episode, with the $PM_{2.5}$ concentration increasing from about 20 μg m^{-3} during the startup stage to more than 300 μg m^{-3} during the maturation stage. The model generally replicates the evolution of the observed $PM_{2.5}$ concentration with an IOA (r) of 0.95 (0.91), but slightly underestimates the $PM_{2.5}$ concentration with an MB (NMB) of -13.0 μg m^{-3} (-8.7%). The simulated diurnal profile of the O_3 concentration is well consistent with observations, with an IOA (r) of 0.94 (0.92), but the model overestimates the O_3 diurnal lows during the maturation stage. Additionally, Figures 8a and 8b also show that both O_3 and $PM_{2.5}$ pollutions occur during the maturation stage in Beijing, as previously reported for non-winter seasons (Jia et al., 2017). The model also exhibits good performance in simulating the temporal variation of NO_2 concentrations, with an IOA (r) of 0.90 (0.81).

3.2.3 Carbonaceous aerosols

The simulated carbonaceous aerosols including POA, SOA, and EC in the model are compared with the hourly observations in Beijing (Figure 9). In general, the temporal variations of the measured carbonaceous aerosols are similar to that of the $PM_{2.5}$ in Figure 8a. The model yields the increasing trend of the POA concentration from the startup to maturation stages compared to the measurements, but cannot well capture the observed spiky peaks, with an IOA (r) of 0.75 (0.58). Figure 9b shows that the observed SOA concentration

265 is remarkably enhanced during the maturation stage, ranging from 30 to 90 μg m^{-3}, which is

266 well predicted by the model. The MB, NMB, IOA, and r for the simulated SOA concentration

267 are -2.1 μg m^{-3}, -6.9%, 0.89, and 0.81, respectively. Although the IOA and r for the simulated

268 EC concentration reach 0.92 and 0.90, respectively, the model considerably underestimates

269 the EC concentration against measurement on October 6 and 7, which is likely caused by the

270 variation in the anthropogenic emissions.

271   Overall, the model performs reasonably in reproducing the observed meteorological

272 fields and the PM$_{2.5}$ and O$_3$ evolutions, and temporal variations of carbonaceous aerosols

273 during the pollution episode, providing a reliable base for the further sensitivity studies.

274 **3.3 Impact of increasing oxidizing capacity on OA**

275   Compared to the REF simulation, when the photolysis frequencies are decreased by 10%,

276 20%, 30%, and 40% in the 4 sensitivity experiments (SEN1~4), respectively, the O$_3$ (OH

277 radical) concentration is correspondingly reduced by 7.4% (9.2%), 15.1% (18.3%), 22.9%

278 (26.9%), and 30.9% (35.7%). It is worth noting that the REF experiment is assumed to

279 represent a situation in autumn with the high AOC, and the SEN1~4 experiments could be

280 regarded as 4 scenarios with the different lower AOC.

281 **3.3.1 OA component changes**

282   Figures 10a and 10b show the variation of POA, SOA, and TOA concentrations as a

283 function of the O$_3$ and OH concentration changes over BTH by differentiating REF and the 4

284 sensitivity experiments, respectively. The SOA level decreases almost linearly with

285 decreasing O$_3$ or OH concentrations, indicating that the AOC plays an important role in the

286 SOA formation over BTH. In the SEN4 experiment with the most reduction of the AOC, the

287 SOA concentration in BTH is reduced by 31.3% or 5.2 μg m^{-3} on average during the episode.

288 The reduction in POA level with decreasing O$_3$ and OH concentrations is generally not

289 substantial, indicating that IVOCs and VOCs are the most important SOA contributors. The

290   TOA (sum of POA and SOA) level also exhibits a decreasing trend with O_3 and OH

291   concentrations. In Figures 10c and 10d, the SOA mass fraction in TOA and OC/EC ratio is

292   considerably reduced as the AOC decreases. The SOA fraction (OC/EC ratio) is about 0.52

293   (6.39) in the REF simulation and almost linearly decreases to around 0.43 (5.49) in the SEN4

294   experiment, indicating a slower aging process of OA with decreasing AOC. The simulated

295   decrease in OC/EC ratio due to reduced AOC could interpret the observed change in OC/EC

296   ratio in Figure 3b to some degree.

297   It is worth noting that the increase in OC/EC ratio potentially influences atmospheric

298   radiation and thermodynamical profiles, through enhancing aerosol scattering and absorption

299   simultaneously (Wang et al., 2013). When the photolysis frequencies are reduced by 30% in

300   the SEN3 experiment, compared to the REF, the downward shortwave radiation is reduced by

301   1.2 W m^{-2} on average in BTH, and the surface temperature is decreased by around 0.016 $^{\circ}$C

302   during daytime. Effects of the AOC change on the temperature profile is not significant, and

303   the daytime temperature decrease in the SEN3 experiment is less than 0.005 $^{\circ}$C within 1 km

304   height from surface.

305   **3.3.2 SOA spatial change in SEN3**

306   Among the 4 experiments, the O_3 change over BTH in SEN3 is close to the observed

307   change (about 30% increase, Figure 3a). Therefore, we further analyze the SOA spatial

308   change in the SEN3 experiment. To illustrate the impacts of the AOC change on the spatial

309   distribution of SOA concentrations in BTH during the haze episode, Figure 11 shows the

310   spatial distributions of the variation in the main oxidant (OH) and SOA concentrations

311   averaged from 4 to 7 October by differentiating REF and the SEN3 experiment. When the

312   photolysis rates are reduced by 30%, the OH concentration over BTH is generally decreased

313   by more than 20%, but the OH variation distribution is not uniform (Figure 11c). The OH

314   decrease is remarkable in the west of Hebei province, compared to the other regions of BTH,

showing the variety of OH sinks and its reservoirs. The most striking decrease in SOA mass occurs in Beijing and surrounding areas, exceeding 8 μg m^{-3} (Figure 11b); while the mass percentage decrease is more noticeable in the west of Hebei province (more than 26%, Figure 11d), which is generally corresponding to the OH reduction. Although OH is the main oxidant in the SOA formation during daytime, the spatial change of SOA concentration is not well consistent with that of the OH concentration, especially for the mass change (Figure 11a). The geographical difference probably results from the spatial distribution variation of anthropogenic and biogenic precursors of SOA. In the middle and east BTH, massive anthropogenic SOA precursors are emitted from residential, transportation and industrial sources; while in the west BTH, biogenic precursor emissions are dominant for the SOA formation, but much less than those from anthropogenic sources in the middle and east BTH (Figure 2).

3.3.3 Changes in the secondary organic aerosol pathways

The spatial decrease in SOA concentration highlights the important influence of AOC change on the SOA formation over BTH. To understand how the SOA components are affected by the changing AOC, we further examine the variation of the SOA formation pathways. The non-traditional SOA module employed in the WRF-Chem model includes 4 SOA formation pathways: oxidation and partitioning of (1) POA treated as semivolatile and co-emitted IVOCs (PSOA), (2) anthropogenic VOCs (ASOA), and (3) biogenic VOCs (BSOA), and (4) heterogeneous reactions of glyoxal and methylglyoxal on aerosol surfaces (HSOA) (Feng et al., 2016; Li et al., 2011b). SOA formation from the 4 pathways in the REF and 4 sensitivity experiments is analyzed to examine the influence of the changing AOC.

Figure 12 shows the changes in SOA concentrations in the 4 sensitivity experiments compared with the REF simulation in Beijing, Tianjin, and Hebei, respectively. The impact of AOC reduction on the 4 pathways and the resulting SOA decreases differ markedly from one

another. Since the oxidation and partitioning of semivolatile POA and co-emitted IVOCs contribute the most to the SOA concentration (Feng et al., 2016), the most substantial SOA decrease occurs in the PSOA, followed by the ASOA and BSOA. The decrease from the HSOA in the 4 experiments is negligible, because the HSOA is mainly contributed by the direct emission of glyoxal and methylglyoxal from residential combustion source (Xing et al., 2019).

It should be noted that, the percentage decreases of SOA from the PSOA in Beijing, Tianjin, and Hebei are comparable (Figure 12b, d, and f), although the mass decrease in Beijing is apparently larger than that in Tianjin and Hebei, indicating the ubiquitous effect of AOC on the PSOA over BTH. The SOA decrease from the ASOA in Beijing is more than that in Tianjin and Hebei, which is likely due to higher and concentrated anthropogenic VOCs emissions in Beijing. By contrast, the SOA decreases from the BSOA are all rather small, and compared with Beijing and Hebei, the SOA decrease from BSOA in Tianjin is even less. In the northwestern part of BTH, the widely distributed forests emit abundant VOCs; whereas the biogenic VOC emissions in Tianjin are much lower owing to a less vegetation cover. In the SEN3 experiment, the SOA decreases in the PSOA, ASOA, and BSOA are 28%, 8%, and 1% in Beijing, respectively, and slightly less than those in Tianjin and Hebei.

4 Summary and conclusions

Observations have revealed substantial increase in O_3 concentrations (about 30%) over BTH and in the ratio of organic carbon (OC) to elemental carbon (EC) in Beijing during the autumn from 2013 to 2015, indicating enhanced AOC and SOA formation. We simulate a 6-day haze episode in BTH from 3 to 8 October 2015 using the WRF-Chem model, as a case study, to explore the influence of the increasing AOC on the SOA formation in BTH.

Generally, the model performs reasonably well in predicting the temporal variations of

365 the temperature, relative humidity, wind speed and direction at 4 meteorological stations in

366 BTH. The spatial distributions of $PM_{2.5}$ and O_3 concentrations over BTH and the temporal

367 variations of $PM_{2.5}$, O_3, NO_2, and carbonaceous aerosols including POA, SOA, and EC in

368 Beijing are also well reproduced against measurements.

369 Four sensitivity experiments with different reductions in the AOC show that changing

370 AOC substantially affects the SOA formation. In the SEN4 scenario, characterized by a 30.9%

371 (35.7%) decrease in O_3 (OH) concentration, the SOA concentration is reduced by 31.3% and

372 the SOA mass fraction in TOA is reduced from 0.52 to 0.43. Spatially, the SOA reduction is

373 ubiquitous over BTH, but the spatial relationship between the SOA concentration and AOC is

374 dependent on the SOA precursor distribution. Among the 4 pathways of the SOA formation

375 in the non-traditional SOA module, the largest SOA reduction in the reduced AOC

376 environment occurs in the PSOA, followed by the ASOA and BSOA. By contrast, the SOA

377 reduction in the HSOA is negligible.

378 Although the model reasonably reproduces the observed meteorological fields and

379 chemical species in BTH, model discrepancies still exist, especially for the $PM_{2.5}$ simulation

380 in Shandong. More studies need to be performed to improve the model simulation and

381 evaluate the impact of AOC change on SOA formation using more accurate meteorological

382 fields and updated anthropogenic emissions.

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384

385 *Author contribution.* Guohui Li, as the contact author, provided the ideas and financial

386 support, verified the conclusions, and revised the paper. Tian Feng conducted a research,

387 designed the experiments, carried the methodology out, performed the simulation, processed

388 the data, prepared the data visualization, and prepared the manuscript with contributions from

389 all authors. Shuyu Zhao and Naifang Bei provided the treatment of meteorological data,

analyzed the study data, validated the model performance, and reviewed the manuscript. Suixin Liu, Yang Qian, Yichen Wang, and Qingchuan Yang provided the observation data used in the study, synthesized the observation, and reviewed the paper. Jiarui Wu, Xia Li, and Lang Liu analyzed the initial simulation data, visualized the model results and reviewed the paper. Weijian Zhou and Junji Cao provided critical reviews pre-publication stage.

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656 Table 1 Anthropogenic emissions of various species in the simulation domain in October
657 2015 (Unit: Mton month^{-1})
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Species	NOx	SO$_2$	NH$_3$	CO	VOC	OC	EC
Beijing	0.31	0.02	0.05	0.66	1.51	0.03	0.01
Tianjin	0.24	0.09	0.05	0.09	2.8	0.05	0.01
Hebei	2.21	0.7	0.62	3.59	21.59	0.41	0.06
Domain	14.21	7.1	4.45	22.19	124.71	2.56	0.3

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664   Table 2 WRF-Chem model configuration

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Item	Configuration
Period	3 ~ 8 October 2015
Regions	Beijing-Tianjin-Hebei, China
Domain center	116°E, 38°N
Domain size	1200 km × 1200 km
Horizontal resolution	6 km × 6 km
Vertical resolution	35 vertical levels with a stretched vertical grid with spacing ranging from 50 m near surface, to 500 m at 2.5 km and 1 km above 14 km
Microphysics scheme	WRF Single-Moment 6-class scheme (Hong and Lim, 2006)
Boundary layer scheme	MYJ TKE scheme (Janjić, 2002)
Surface layer scheme	MYJ surface scheme (Janjić, 2002)
Land-surface scheme	Noah land surface model (Chen and Dudhia, 2001)
Longwave radiation scheme	New Goddard scheme (Chou et al., 2001)
Shortwave radiation scheme	New Goddard scheme (Chou and Suarez, 1999)
Meteorological boundary and initial condition	NCEP 1° × 1° reanalysis data
Chemical boundary and initial condition	MOZART 6-h output (Horowitz et al., 2003)
Anthropogenic emission inventory	SAPRC99 chemical mechanism emissions (Zhang et al., 2009), base year: 2013
Biogenic emission inventory	MEGAN model developed by Guenther et al. (2006)
Spin-up time	1.5 days

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671   Table 3 Description of the reference simulation and sensitivity experiments
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Case ID	Description
REF	The reference simulation constrained by observations
SEN1	10% decrease in photolysis frequencies
SEN2	20% decrease in photolysis frequencies
SEN3	30% decrease in photolysis frequencies
SEN4	40% decrease in photolysis frequencies

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Figure 1 Model domain with the topography. The black circles denote the locations of the cities with ambient air quality monitoring sites, and the size of the circles represents the number of sites in each city. The white triangles show the location of the meteorological stations in Beijing, Tianjin, Shijiazhuang, and Baoding. The light blue and pink dots in Beijing show the observation sites with the POA/SOA (NCNT) and OC/EC (CRAES) measurements, respectively.

Figure 2 Geographic distributions of anthropogenic emissions of (a) volatile organic compounds and (b) organic carbon in October in the simulation domain. The black lines present provincial boundaries in China.

Figure 3 (a) Measured concentrations of O_3, NO_2, SO_2, CO, and $PM_{2.5}$ in BTH averaged during 15 September ~ 14 November from 2013 to 2017, and (b) OC and EC concentrations (bars) and OC/EC ratios (line) measured in Beijing averaged during 15 September ~ 14 November from 2013 to 2015.

Figure 4 Simulated (red curves) and observed (black dots) temporal profiles of surface (a-d) temperature and (e-h) relative humidity in (a, e) Beijing, (b, f) Tianjin, (c, g) Shijiazhuang, and (d, h) Baoding from 3 to 8 October 2015.

Figure 5 Simulated (red curves) and observed (black dots) temporal profiles of surface (a-d) wind speed and (e-h) wind direction in (a, e) Beijing, (b, f) Tianjin, (c, g) Shijiazhuang, and (d, h) Baoding from 3 to 8 October 2015.

Figure 6 Spatial distributions of the modeled (colored shadings) and observed (colored dots) surface daily $PM_{2.5}$ concentration from 3 to 8 October 2015. Black arrows show the simulated surface winds.

Figure 7 Spatial distributions of the modeled (colored shadings) and observed (colored dots) surface O_3 concentration at 14:00 (local time) from 3 to 8 October 2015. Black arrows show the simulated surface winds.

Figure 8 Diurnal variations of the modeled (red curves) and observed (black dots) surface (a) $PM_{2.5}$, (b) O_3, and (c) NO_2 concentrations averaged over 12 ambient monitoring stations in Beijing from 3 to 8 October 2015.

Figure 9 Diurnal variations of the modeled (red curves) and observed (black dots) surface submicron (a) POA and (b) SOA concentrations at the NCNT station, and (c) EC concentration in $PM_{2.5}$ at the CRAES station in Beijing from 3 to 8 October 2015.

Figure 10 Impacts of changes in the AOC on organic aerosol components in BTH in 4 sensitivity experiments. (a) Concentration changes of POA, SOA, and TOA *versus* O_3, (b) Concentration changes of POA, SOA, and TOA *versus* OH, (c) SOA fraction in TOA *versus* OH concentration change, and (d) OC/EC ratio *versus* OH concentration change.

Figure 11 Spatial distributions of changes in (a, c) OH and (b, d) SOA concentrations averaged from 4 to 7 October 2015 in the SEN3 experiment compared to the REF simulation (SEN3 – REF).
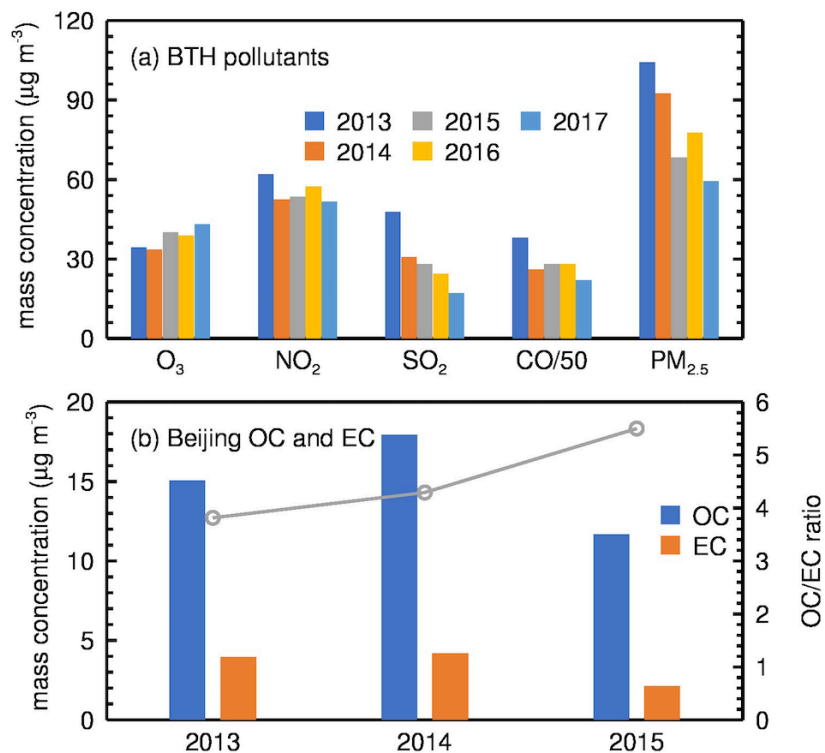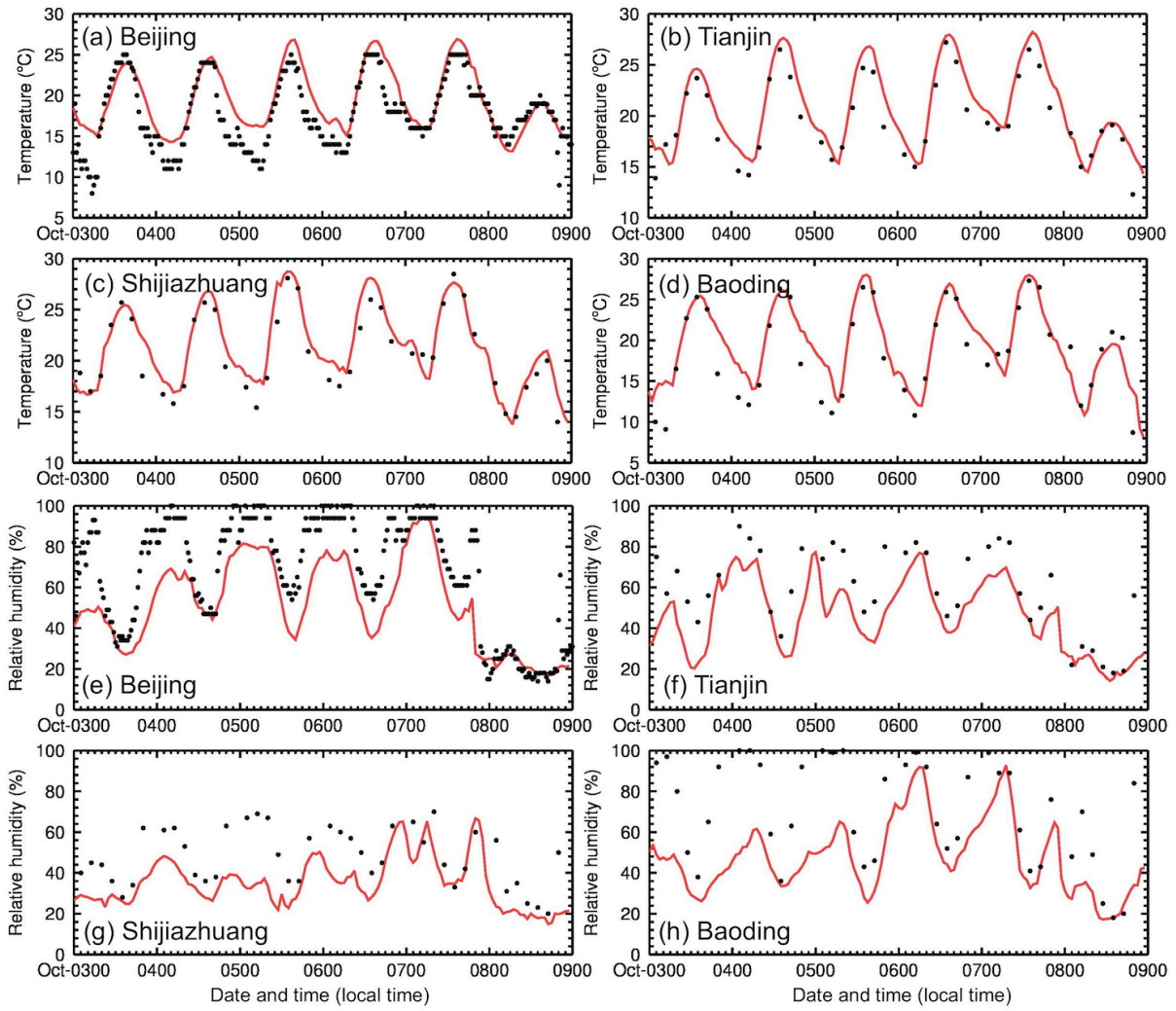
719   Figure 12 Histogram showing the decreases of SOA from various pathways in (a, b) Beijing,
720   (c, d) Tianjin, and (e, f) Hebei in the sensitivity experiments compared to the REF
721   simulation (SENx – REF, x = 1, 2, 3, and 4). PSOA: oxidation and partitioning of
722   semivolatile POA and co-emitted IVOCs; ASOA: oxidation and partitioning of
723   anthropogenic VOCs; BSOA: oxidation and partitioning of biogenic VOCs; HSOA:
724   heterogeneous reactions of glyoxal and methylglyoxal on aerosol surfaces.

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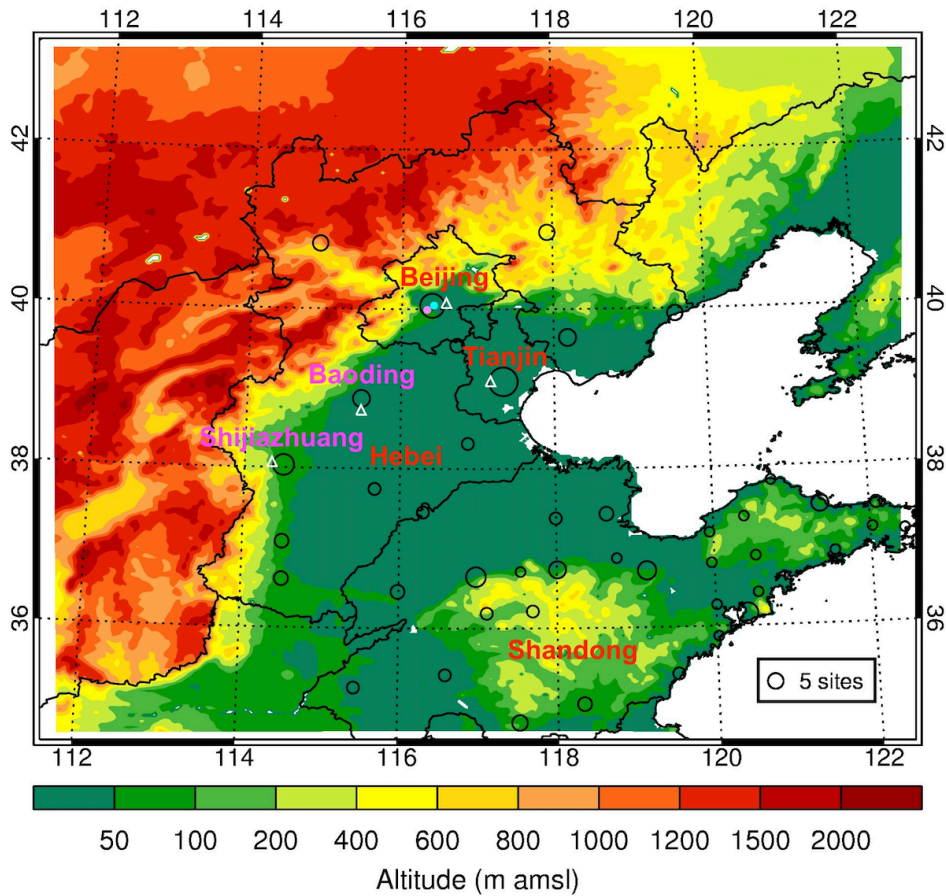
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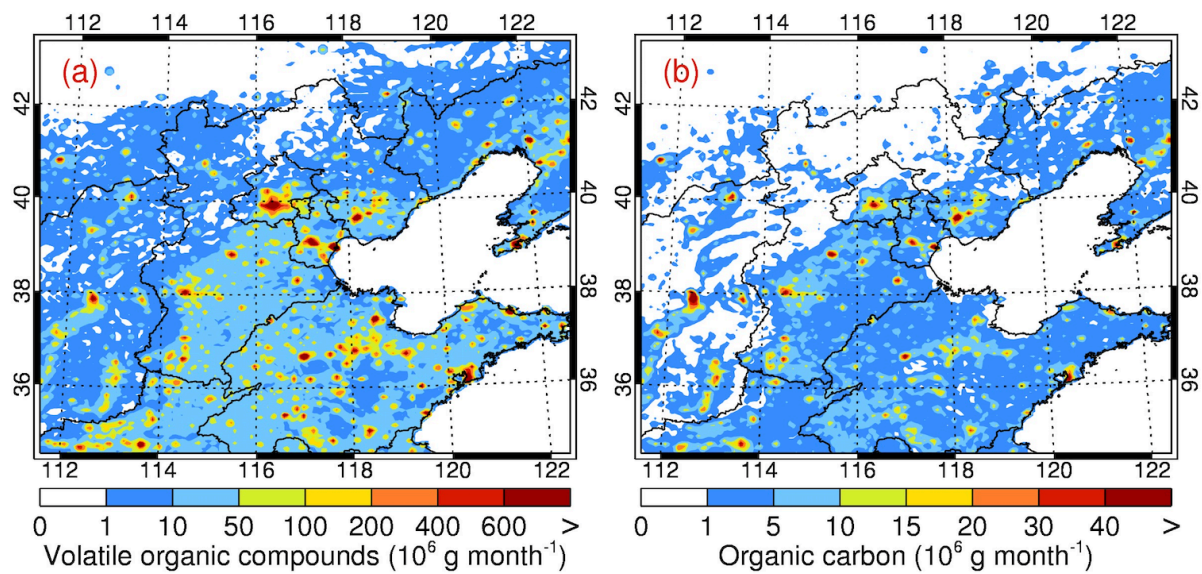
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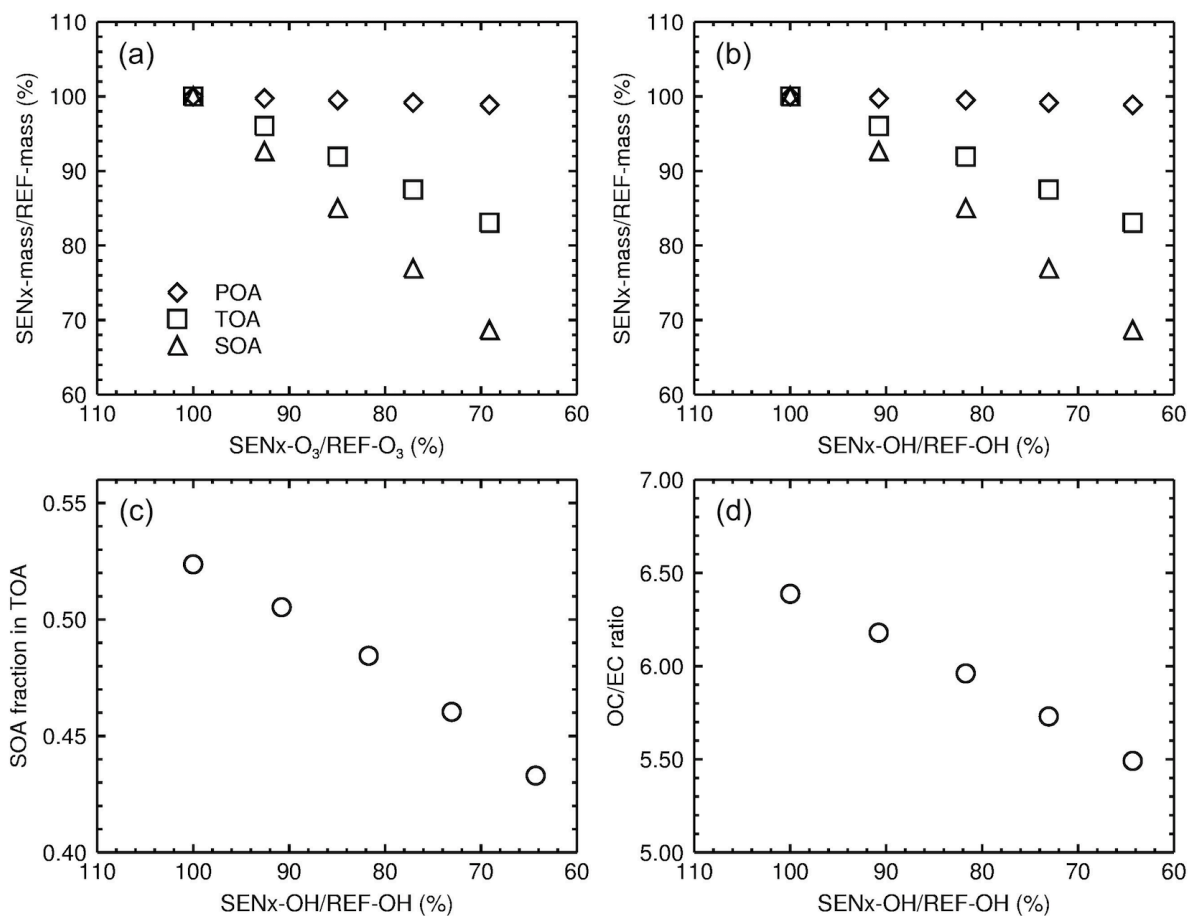
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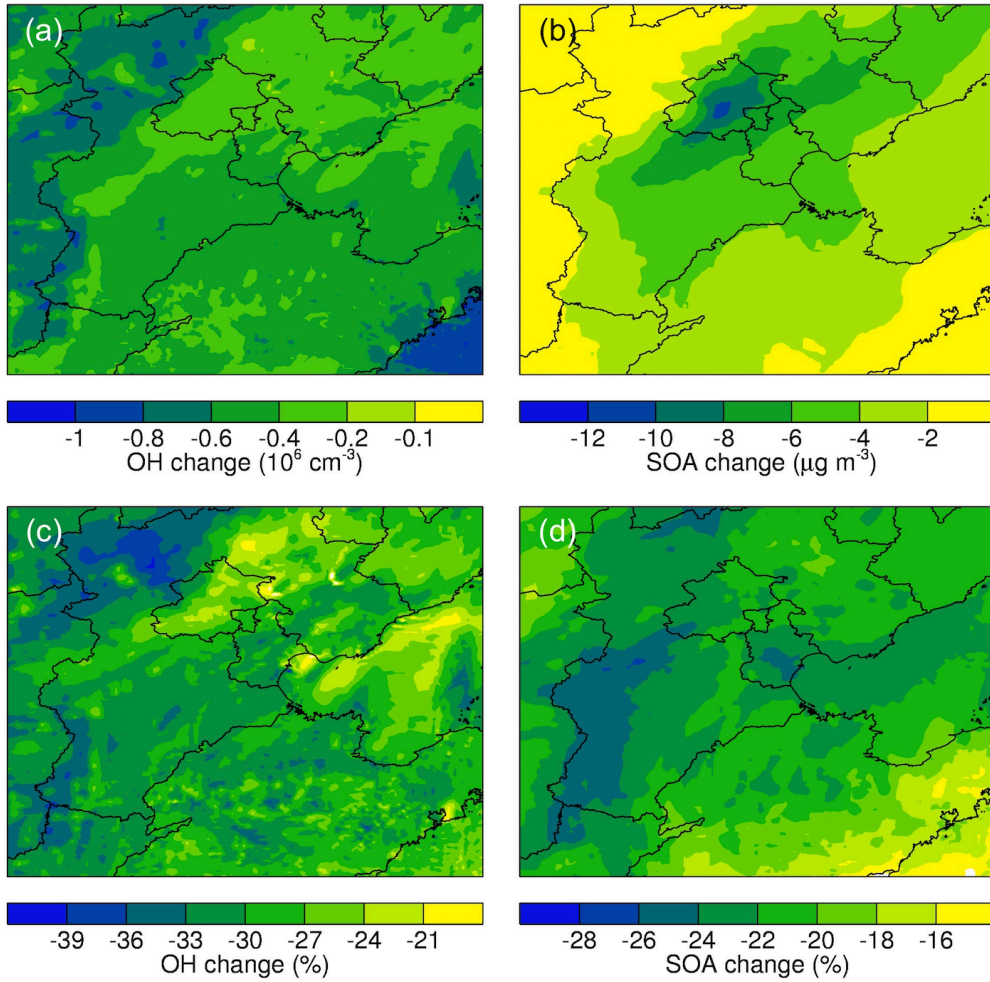
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812 Figure 9 Diurnal variations of the modeled (red curves) and observed (black dots) surface
813 submicron (a) POA and (b) SOA concentrations at the NCNT station, and (c) EC
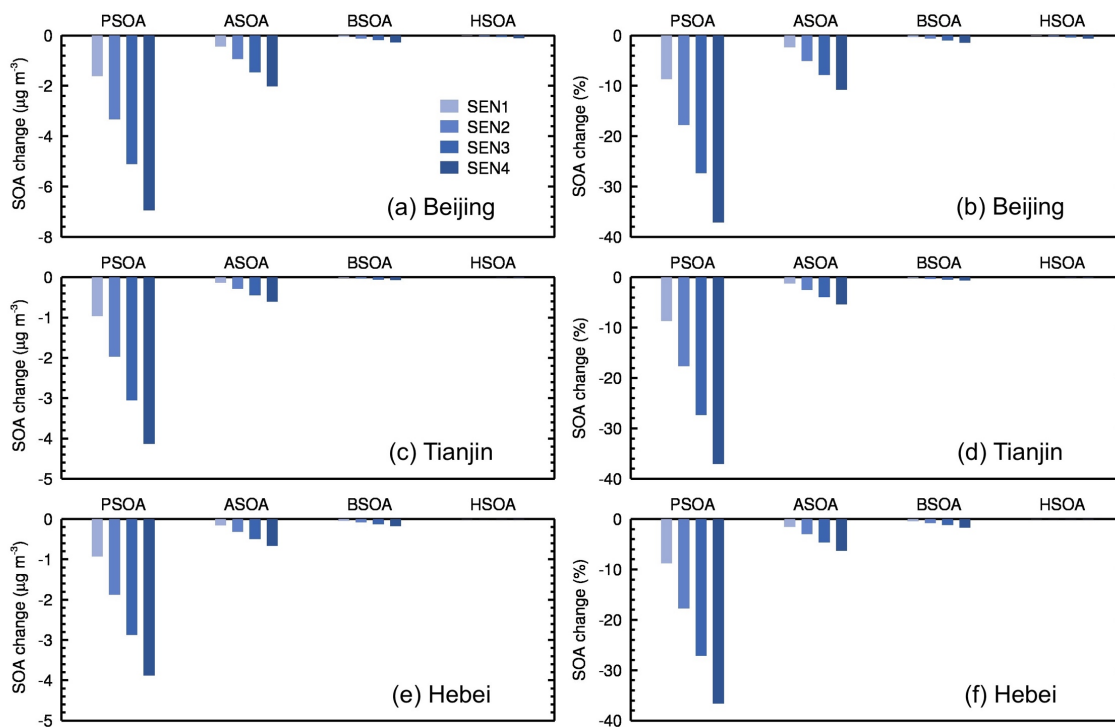814 concentration in $PM_{2.5}$ at the CRAES station in Beijing from 3 to 8 October 2015.
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