- Secondary organic aerosol enhanced by increasing atmospheric oxidizing capacity in 1 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 atmospheric oxidizing capacity (AOC) and secondary organic aerosol (SOA) formation. To 25 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 O₃ 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 O₃ concentrations over BTH and the temporal variations of PM_{2.5}, 30 O₃, NO₂, 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 sensitivity case characterized by a 31% O₃ decrease (or 36% OH decrease) reduces the SOA 32 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 AOC is reduced, the SOA from oxidation and partitioning of semi-volatile POA and 37 38 co-emitted intermediate volatile organic compounds (IVOCs) decreases remarkably, followed by those from anthropogenic and biogenic VOCs. Meanwhile, the SOA decrease in the 39 40 irreversible uptake of glyoxal and methylglyoxal on aerosol surfaces is negligible.

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421 1 Introduction

43 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 44 45 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 46 47 not only deteriorate air quality and visibility (Cao et al., 2012a; Feng et al., 2016; Seinfeld 48 and Pandis, 2006), but also threat the public health and ecosystem (Cao et al., 2012b; Tie et 49 al., 2016). In addition, PM_{2.5} also modulates the energy budget of the earth system directly 50 through absorbing and scattering the incident solar radiation and indirectly via acting as cloud 51 condensation nuclei (CCN) and ice nuclei (IN) and subsequently altering cloud albedo and 52 lifetime (Li et al., 2008; 2009; Wang et al., 2013; 2016b; 2018; Zhou et al., 2017).

53 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 54 55 have confirmed a large mass fraction of OA in ambient PM2.5 in various Chinese cities. For 56 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 57 58 haze episodes. Positive matrix factorization (PMF) analyses of the aerosol chemical 59 speciation monitor (ACSM) measurements in Beijing have shown that OA contributes 40% 60 and 52% of refractory submicron particulate matters in summer 2011 and winter 2012, 61 respectively (Sun et al., 2013; 2012). Over BTH, Huang et al. (2017) have demonstrated that 62 OA constitutes the most important part in the major chemical components of gravimetric 63 PM_{2.5} (20~25%) based on measurements at 3 urban sites from June 2014 to April 2015.

64 OA is traditionally categorized into primary and secondary organic aerosols (referred to 65 as POA and SOA, respectively) in terms of its source and formation in the atmosphere. POA 66 is the OA directly emitted into the atmosphere, and SOA is formed through a series of 67 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., 68 69 2011b; Tsimpidi et al., 2010). SOA precursors mainly include volatile organic compounds 70 (VOCs) emitted from anthropogenic and biogenic sources (Odum et al., 1996; Pankow, 1994), 71 primary organic gases (POG) emitted or formed in the evaporation of POA, and intermediate 72 VOCs (IVOCs) co-emitted with the POA (Lipsky and Robinson, 2006; Robinson et al., 2007; 73 Shrivastava et al., 2006). The pathway of SOA formation is illustrated as follows (Li et al., 74 2011b; Robinson et al., 2007):

75
$$VOCs_{(g)} + oxidants \rightarrow OVOCs_{(g)} \leftrightarrow SOA_{(p)}$$
 (R1)

76
$$IVOCs_{(g)} + OH \rightarrow OIVOCs \leftrightarrow SOA_{(p)}$$
 (R2)

77
$$POA_{(p)} \leftrightarrow POG_{(g)} + OH \to OPOG_{(g)} \leftrightarrow SOA_{(p)}$$
 (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 (O₃), hydroxyl radical (OH) and nitrate radical (NO₃). 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, O₃ concentrations have dramatically increased in eastern China. For example, Cheng et al. (2016) have reported an increasing trend of the daily maximum 1h O₃ concentration over Beijing from 2004 to 2015. Ma et al. (2016) have observed a significant increase of surface O₃ 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

concentration has been significantly reduced by 27.5%, 17.4%, and 14.0% in Beijing, Tianjin, 92 and Hebei, respectively, from 2013 to 2017. The increasing O₃ concentration has become a 93 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 O₃ concentration has increased by 23% from 2013 to 2015 (Wu et al., 2017). 98 Such an increasing trend of O₃ 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

1072 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 model (Grell et al., 2005) developed by Li et al. (2011b; 2011a; 2012; 2010). The model 110 111 includes a flexible gas phase chemical module and the Models-3 community multiscale air quality (CMAQ) aerosol module (Binkowski and Roselle, 2003). The photolysis rates are 112 113 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 the volatility basis-set (VBS) method (Donahue et al., 2006; Robinson et al., 2007) is 115 incorporated into the model to simulate organic aerosols. In this module, POA is distributed 116

117 in logarithmically spaced volatility bins and presumed to be semi-volatile and photochemically reactive (Li et al., 2011b). The module uses 9 surrogate species with 118 saturation concentration ranging from 10^{-2} to 10^{6} µg m⁻³ at room temperature to represent 119 120 POA compositions (Shrivastava et al., 2008). IVOCs, co-emitted with the POA but in the gas phase, are also oxidized by OH to form SOA. In addition, the SOA formation from glyoxal 121 122 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 Ozone Chemistry Aerosol Radiation and Transport model) dust module is used to estimate 126 the emission, transport, dry deposition, and gravitational settling of dust (Ginoux et al., 2001). 127 128 The biomass burning emissions are from the Fire Inventory from NCAR (FINN) (Wiedinmyer et al., 2011; 2006). The dry deposition of chemical species is parameterized 129 following Wesely (1989) and the wet deposition is calculated using the method in the CMAQ 130 module (Binkowski and Roselle, 2003). Specifically, the surface and upper air observational 131 132 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.

A severe haze episode from 3 to 8 October 2015 in BTH with high O_3 and $PM_{2.5}$ concentrations is simulated. The model is configured with one single domain which is centered at 116°E and 38°N with grid spacing of 6 km×6 km (200×200 grid cells). Thirty-five stretched vertical levels with spacing ranging from about 30 m near surface, to 500 m at 2.5 km, and 1 km above 14 km are used in the model configuration. The monthly average anthropogenic emission inventory is developed by Zhang et al. (2009) and Li et al. (2017c), with the base year of 2013, including agriculture, industry, power generation,

residential, and transportation sources. The temporal resolution of emissions used in 142 simulations is 1 hour, and the temporal allocation for different sources follows those in Zhang 143 144 et al. (2009). Figure 2 presents the spatial distributions of anthropogenic volatile organic compounds (VOCs) and organic carbon (OC) emissions in October, showing high emissions 145 in urban areas. The emissions of various species in Beijing, Tianjin, Hebei, and the entire 146 147 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**

Measurement data used in this study include the hourly concentrations of O₃, NO₂, SO₂, 151 CO, and PM_{2.5} from ambient monitoring stations of China's Ministry of Environment and 152 153 Ecology (China MEE) and hourly OC and EC concentrations in PM2.5 measured hourly at Chinese Research Academy of Environmental Sciences (CRAES) using a Sunset OC/EC 154 155 Analyzer (RT-4, Sunset Lab, USA). The OC/EC analyzer has been widely used in ambient and indoor OC/EC detections in China (Liu et al., 2018; Wei et al., 2014). In addition, hourly 156 157 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) in Beijing. 159

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

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. \overline{P} and \overline{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

1812 3 Results and discussion

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

Figure 3a shows the annual variation of measured mean concentrations of O₃, NO₂, SO₂, CO, and PM_{2.5} over BTH in the autumn from 2013 to 2017. To better present the pollution characteristics in autumn, the observations from 15 September to 14 November are selected in this study, which avoids the heating period (starting from 15 November) in northern China. Obvious decreasing trends in NO₂, SO₂, CO, and PM_{2.5} concentrations during recent years are observed since the implementation of APPCAP (Figure 3a). The O₃ concentration, however, has increased by about 30% during the same period. Such an O₃ increase indicates a

(2)

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 measured in Beijing in the autumns from 2013 to 2015 (Figure 3b). The measured OC/EC 199 200 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 AOC, which enhances the SOA formation. Secondly, the increase might be caused by the 202 203 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**

Model performance in meteorological fields is crucial for the simulation of air pollutants (Bei et al., 2010; 2012; 2017). Figures 4 and 5 present the simulated temporal variations of the surface temperature, relative humidity, wind speed, and wind direction against observations at 4 meteorological stations (Beijing, Tianjin, Shijiazhuang, and Baoding, 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 wind with a maximum speed exceeding 10 m s⁻¹ and the wind direction at noon on 8 October 224 in Beijing. Overall, the model still generally captures the temporal variations of wind 225 226 directions in the 4 cities.

227 **3.2.2 PM_{2.5}, O₃, and NO₂**

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 October), (3) maturation (5-7 October), and (4) dissipation (8 October). On 3 October, the 231 232 haze formed in Shandong and southern BTH, accompanied by weak winds near the surface (< 2 m s⁻¹). On 4 October, the southerly wind prevailed, causing trans-boundary transport of 233 234 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 the PM_{2.5} concentration in Shandong province. 238

Figure 7 shows the observed and simulated spatial distribution of peak O₃ concentrations

at 14:00 (local time, hereafter) during the episode. Similar to $PM_{2.5}$, the high O₃ concentration first occurred in Shandong province on 3 October, and propagated to BTH on 4 October. During the maturation period, the O₃ level in BTH still remained high. The simulated spatial distributions of O₃ concentrations generally agree well with the observations during the four stages, but underestimation or overestimation still exists.

245 Figure 8 shows the temporal variations of the simulated and observed surface PM_{2.5}, O₃, 246 and NO₂ concentrations averaged over 12 ambient monitoring stations in Beijing. The 247 simulated and observed PM_{2.5} temporal pattern clearly shows the 4 stages of the haze episode, 248 with the PM_{2.5} concentration increasing from about 20 μ g m⁻³ during the startup stage to more than 300 µg m⁻³ during the maturation stage. The model generally replicates the evolution of 249 the observed PM_{2.5} concentration with an IOA (r) of 0.95 (0.91), but slightly underestimates 250 251 the PM_{2.5} concentration with an MB (NMB) of -13.0 μ g m⁻³ (-8.7%). The simulated diurnal profile of the O_3 concentration is well consistent with observations, with an IOA (r) of 0.94 252 253 (0.92), but the model overestimates the O₃ diurnal lows during the maturation stage. 254 Additionally, Figures 8a and 8b also show that both O₃ and PM_{2.5} pollutions occur during the 255 maturation stage in Beijing, as previously reported for non-winter seasons (Jia et al., 2017). 256 The model also exhibits good performance in simulating the temporal variation of NO₂ concentrations, with an IOA (*r*) of 0.90 (0.81). 257

258 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

- is remarkably enhanced during the maturation stage, ranging from 30 to 90 μ g m⁻³, which is
- 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.

Overall, the model performs reasonably in reproducing the observed meteorological fields and the $PM_{2.5}$ and O_3 evolutions, and temporal variations of carbonaceous aerosols during the pollution episode, providing a reliable base for the further sensitivity studies.

274 3.3 Impact of increasing oxidizing capacity on OA

Compared to the REF simulation, when the photolysis frequencies are decreased by 10%, 20%, 30%, and 40% in the 4 sensitivity experiments (SEN1~4), respectively, the O₃ (OH radical) concentration is correspondingly reduced by 7.4% (9.2%), 15.1% (18.3%), 22.9% (26.9%), and 30.9% (35.7%). It is worth noting that the REF experiment is assumed to represent a situation in autumn with the high AOC, and the SEN1~4 experiments could be 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 function of the O₃ and OH concentration changes over BTH by differentiating REF and the 4 283 284 sensitivity experiments, respectively. The SOA level decreases almost linearly with 285 decreasing O₃ 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 $5.2 \ \mu g \ m^{-3}$ on average during the episode. The reduction in POA level with decreasing O₃ and OH concentrations is generally not 288 289 substantial, indicating that IVOCs and VOCs are the most important SOA contributors. The TOA (sum of POA and SOA) level also exhibits a decreasing trend with O₃ and OH concentrations. In Figures 10c and 10d, the SOA mass fraction in TOA and OC/EC ratio is considerably reduced as the AOC decreases. The SOA fraction (OC/EC ratio) is about 0.52 (6.39) in the REF simulation and almost linearly decreases to around 0.43 (5.49) in the SEN4 experiment, indicating a slower aging process of OA with decreasing AOC. The simulated decrease in OC/EC ratio due to reduced AOC could interpret the observed change in OC/EC ratio in Figure 3b to some degree.

It is worth noting that the increase in OC/EC ratio potentially influences atmospheric 297 298 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 the SEN3 experiment, compared to the REF, the downward shortwave radiation is reduced by 300 301 1.2 W m⁻² on average in BTH, and the surface temperature is decreased by around 0.016 °C during daytime. Effects of the AOC change on the temperature profile is not significant, and 302 303 the daytime temperature decrease in the SEN3 experiment is less than 0.005 °C within 1 km 304 height from surface.

305 3.3.2 SOA spatial change in SEN3

306 Among the 4 experiments, the O₃ change over BTH in SEN3 is close to the observed 307 change (about 30% increase, Figure 3a). Therefore, we further analyze the SOA spatial change in the SEN3 experiment. To illustrate the impacts of the AOC change on the spatial 308 309 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 by more than 20%, but the OH variation distribution is not uniform (Figure 11c). The OH 313 314 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 315 occurs in Beijing and surrounding areas, exceeding 8 µg m⁻³ (Figure 11b); while the mass 316 317 percentage decrease is more noticeable in the west of Hebei province (more than 26%, Figure 318 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 319 well consistent with that of the OH concentration, especially for the mass change (Figure 320 321 11a). The geographical difference probably results from the spatial distribution variation of 322 anthropogenic and biogenic precursors of SOA. In the middle and east BTH, massive 323 anthropogenic SOA precursors are emitted from residential, transportation and industrial sources; while in the west BTH, biogenic precursor emissions are dominant for the SOA 324 formation, but much less than those from anthropogenic sources in the middle and east BTH 325 326 (Figure 2).

327 **3.3.3** Changes in the secondary organic aerosol pathways

328 The spatial decrease in SOA concentration highlights the important influence of AOC 329 change on the SOA formation over BTH. To understand how the SOA components are 330 affected by the changing AOC, we further examine the variation of the SOA formation 331 pathways. The non-traditional SOA module employed in the WRF-Chem model includes 4 332 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 333 334 (BSOA), and (4) heterogeneous reactions of glyoxal and methylglyoxal on aerosol surfaces 335 (HSOA) (Feng et al., 2016; Li et al., 2011b). SOA formation from the 4 pathways in the REF 336 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).

346 It should be noted that, the percentage decreases of SOA from the PSOA in Beijing, 347 Tianjin, and Hebei are comparable (Figure 12b, d, and f), although the mass decrease in 348 Beijing is apparently larger than that in Tianjin and Hebei, indicating the ubiquitous effect of 349 AOC on the PSOA over BTH. The SOA decrease from the ASOA in Beijing is more than that 350 in Tianjin and Hebei, which is likely due to higher and concentrated anthropogenic VOCs 351 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 352 353 the northwestern part of BTH, the widely distributed forests emit abundant VOCs; whereas 354 the biogenic VOC emissions in Tianjin are much lower owing to a less vegetation cover. In 355 the SEN3 experiment, the SOA decreases in the PSOA, ASOA, and BSOA are 28%, 8%, and 356 1% in Beijing, respectively, and slightly less than those in Tianjin and Hebei.

357

3583 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.

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

the temperature, relative humidity, wind speed and direction at 4 meteorological stations in BTH. The spatial distributions of $PM_{2.5}$ and O_3 concentrations over BTH and the temporal variations of $PM_{2.5}$, O_3 , NO_2 , and carbonaceous aerosols including POA, SOA, and EC in 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 O₃ (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 dependent on the SOA precursor distribution. Among the 4 pathways of the SOA formation 374 375 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 reduction in the HSOA is negligible. 377

Although the model reasonably reproduces the observed meteorological fields and chemical species in BTH, model discrepancies still exist, especially for the $PM_{2.5}$ simulation in Shandong. More studies need to be performed to improve the model simulation and evaluate the impact of AOC change on SOA formation using more accurate meteorological fields and updated anthropogenic emissions.

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Author contribution. Guohui Li, as the contact author, provided the ideas and financial support, verified the conclusions, and revised the paper. Tian Feng conducted a research, designed the experiments, carried the methodology out, performed the simulation, processed the data, prepared the data visualization, and prepared the manuscript with contributions from all authors. Shuyu Zhao and Naifang Bei provided the treatment of meteorological data,

390	analyzed the study data, validated the model performance, and reviewed the manuscript.
391	Suixin Liu, Yang Qian, Yichen Wang, and Qingchuan Yang provided the observation data
392	used in the study, synthesized the observation, and reviewed the paper. Jiarui Wu, Xia Li, and
393	Lang Liu analyzed the initial simulation data, visualized the model results and reviewed the
394	paper. Weijian Zhou and Junji Cao provided critical reviews pre-publication stage.
395	
396	
397	Acknowledgements. This work is financially supported by the National Key R&D Plan
398	(Quantitative Relationship and Regulation Principle between Regional Oxidation Capacity of
399	Atmospheric and Air Quality (2017YFC0210000)) and National Research Program for Key
400	Issues in Air Pollution Control (DQGG0105). Tian Feng is supported by National Natural
401	Science Foundation of China (no. 41703127, 41430424, 41661144020).
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657 658 Table 1 Anthropogenic emissions of various species in the simulation domain in October 2015 (Unit: Mton month⁻¹)

Species	<mark>NOx</mark>	SO ₂	NH3	CO	VOC	<mark>OC</mark>	<mark>EC</mark>
Beijing	<mark>0.31</mark>	<mark>0.02</mark>	<mark>0.05</mark>	<mark>0.66</mark>	<mark>1.51</mark>	<mark>0.03</mark>	<mark>0.01</mark>
<mark>Tianjin</mark>	<mark>0.24</mark>	<mark>0.09</mark>	<mark>0.05</mark>	<mark>0.09</mark>	<mark>2.8</mark>	<mark>0.05</mark>	<mark>0.01</mark>
Hebei	<mark>2.21</mark>	<mark>0.7</mark>	<mark>0.62</mark>	<mark>3.59</mark>	<mark>21.59</mark>	<mark>0.41</mark>	<mark>0.06</mark>
<mark>Domain</mark>	<mark>14.21</mark>	<mark>7.1</mark>	<mark>4.45</mark>	<mark>22.19</mark>	<mark>124.71</mark>	<mark>2.56</mark>	<mark>0.3</mark>

64 Table 2 WRF-Chem model configuration

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	$6 \text{ km} \times 6 \text{ km}$
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 $1^{\circ} \times 1^{\circ}$ 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

Table 3 Description of the reference simulation and sensitivity experiments

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	Case ID	Description
-	REF_	The reference simulation constrained by observations
	<mark>SEN1</mark>	10% decrease in photolysis frequencies
	<mark>SEN2</mark>	20% decrease in photolysis frequencies
	<mark>SEN3</mark>	30% decrease in photolysis frequencies
_	<mark>SEN4</mark>	40% decrease in photolysis frequencies
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678		Figure captions
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680 681 682 683 684 685	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.
686 687 688	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.
689 690 691 692	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.
693 694 695	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.
696 697 698	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.
699 700 701	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.
702 703 704	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.
705 706 707	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.
708 709 710	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.
711 712 713 714 715	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 <i>versus</i> O_3 , (b) Concentration changes of POA, SOA, and TOA <i>versus</i> OH, (c) SOA fraction in TOA <i>versus</i> OH concentration change, and (d) OC/EC ratio <i>versus</i> OH concentration change.
716 717 718	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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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.

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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
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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 lines) 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 lines) 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 O₃ 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) O₃, and (c) NO₂ 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 O₃, (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.



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833 Figure 11 Spatial distributions of changes in (a, c) OH and (b, d) SOA concentrations
834 averaged from 4 to 7 October 2015 in the SEN3 experiment compared to the REF simulation
835 (SEN3 – REF).





Figure 12 Histogram showing the decreases of SOA from various pathways in (a, b) Beijing, (c, d) Tianjin, and (e, f) Hebei in the sensitivity experiments compared to the REF simulation (SENx – REF, x = 1, 2, 3, and 4). PSOA: oxidation and partitioning of semivolatile POA and co-emitted IVOCs; ASOA: oxidation and partitioning of anthropogenic VOCs; BSOA: oxidation and partitioning of biogenic VOCs; HSOA: heterogeneous reactions of glyoxal and methylglyoxal on aerosol surfaces.

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