Secondary organic aerosol enhanced by increasing atmospheric oxidizing capacity in Beijing-Tianjin-Hebei (BTH), China

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Abstract. The implementation of the Air Pollution Prevention and Control Action Plan in China since 2013 has profoundly altered the ambient pollutants in the Beijing-Tianjin-Hebei region (BTH). Here we show observations of substantially increased O3 concentrations (about 30%) and a remarkable increase in the ratio of organic carbon (OC) to elemental 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 explore the impacts of increasing AOC on the SOA formation, a severe air pollution episode from 3 to 8 October 2015 with high O3 and PM2.5 concentrations is simulated using the WRF-Chem model. The model performs reasonably well in simulating the spatial distributions of PM2.5 and O3 concentrations over BTH and the temporal variations of PM2.5, O3, NO2, OC, and EC concentrations in Beijing compared to measurements. Sensitivity 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 level by about 30% and the SOA fraction in total organic aerosol by 17% (from 0.52 to 0.43, dimensionless). Spatially, the SOA decrease caused by reduced AOC is ubiquitous in BTH, but the spatial relationship between SOA concentrations and the AOC is dependent on the 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 co-emitted intermediate volatile organic compounds (IVOCs) decreases remarkably, followed by those from anthropogenic and biogenic VOCs. Meanwhile, the SOA decrease in the 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):

\[
\text{VOCs}_{(g)} + \text{oxidants} \rightarrow \text{OVOCs}_{(g)} \leftrightarrow \text{SOA}_{(p)} \quad (R1)
\]

\[
\text{IVOCs}_{(g)} + \text{OH} \rightarrow \text{OIVOCs} \leftrightarrow \text{SOA}_{(p)} \quad (R2)
\]

\[
\text{POA}_{(p)} \leftrightarrow \text{POG}_{(g)} + \text{OH} \rightarrow \text{OPOG}_{(g)} \leftrightarrow \text{SOA}_{(p)} \quad (R3)
\]

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
concentration has been significantly reduced by 27.5%, 17.4%, and 14.0% in Beijing, Tianjin, and Hebei, respectively, from 2013 to 2017. The increasing O₃ concentration has become a new culprit for the deterioration of the air quality in eastern China (Li et al., 2017b; Wu et al., 2017). Li et al. (2017b) have reported that the O₃ concentration has increased by 10% from 2013 to 2015 averaged over 65 cities of eastern China during April ~ September. In Beijing, the summertime O₃ concentration has increased by 23% from 2013 to 2015 (Wu et al., 2017). Such an increasing trend of O₃ concentrations reflects an enhancement of the atmospheric oxidizing capacity (AOC), which, as expected, potentially influences the SOA formation and OA components. Therefore, it is imperative to evaluate the impact of the increasing AOC on the SOA formation over BTH.

The objective of this study is to evaluate the impact of the increasing AOC on OA components in BTH (Figure 1) during a haze episode in the autumn of 2015 using the WRF-Chem model. Model and configuration are described in Sect. 2; the results and discussion are presented in Sect. 3. The conclusions are drawn in Sect. 4.

2 Model and method

2.1 WRF-Chem model and configuration

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 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 calculated using the FTUV module (Li et al., 2005; Tie et al., 2003) which takes into account 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 incorporated into the model to simulate organic aerosols. In this module, POA is distributed
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 saturation concentration ranging from $10^{-2}$ to $10^6 \mu g m^{-3}$ at room temperature to represent 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 and methylglyoxal is included in the module, which is parameterized as a first-order irreversible uptake on aerosol surface with a reactive uptake coefficient of $3.7 \times 10^{-3}$ (Volkamer et al., 2007; Zhao et al., 2006). Inorganic aerosols are calculated by the 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 the emission, transport, dry deposition, and gravitational settling of dust (Ginoux et al., 2001). 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 following Wesely (1989) and the wet deposition is calculated using the method in the CMAQ module (Binkowski and Roselle, 2003). Specifically, the surface and upper air observational wind fields from China Meteorological Administration (CMA) during the study period are assimilated using the four-dimensional data assimilation (FDDA) method to better simulate 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
simulations is 1 hour, and the temporal allocation for different sources follows those in Zhang
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
in urban areas. The emissions of various species in Beijing, Tianjin, Hebei, and the entire
domain in October 2015 are summarized in Table 1. Biogenic emissions are calculated online
using the MEGAN (Model of Emissions of Gases and Aerosol from Nature) model (Guenther
et al., 2006). The model configuration is presented in Table 2.

2.2 Pollutant measurements

Measurement data used in this study include the hourly concentrations of O₃, NO₂, SO₂,
CO, and PM₂.₅ from ambient monitoring stations of China’s Ministry of Environment and
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
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
submicron POA and SOA concentrations are obtained from the ACSM measurement
analyzed using the PMF method at National Center for Nanoscience and Technology (NCNT)
in Beijing.

2.3 Model simulations

We define the simulation with the AOC in October 2015 as the reference (REF). The
model result in REF is compared with the observations to evaluate the model performance.
To examine the impact of increasing AOC on OA components, we perform 4 sensitivity
experiments (SEN1~4) by varying AOC. Compared with the REF simulation, we decrease all
the photolysis frequencies by 10%, 20%, 30%, and 40%, respectively, in the model
simulations.
2.4 Statistic method

The mean bias (MB), normalized mean bias (NMB), root mean square error (RMSE), index of agreement (IOA), and linear Pearson correlation coefficient (r) are selected to evaluate the WRF-Chem model simulations against observations.

\[ MB = \frac{1}{N} \sum_{i=1}^{N} (P_i - O_i) \]  
\[ NMB = \frac{\sum_{i=1}^{N} (P_i - O_i)}{\sum_{i=1}^{N} O_i} \times 100\% \]  
\[ RMSE = \left[ \frac{1}{N} \sum_{i=1}^{N} (P_i - O_i)^2 \right]^{\frac{1}{2}} \]  
\[ IOA = 1 - \frac{\sum_{i=1}^{N} (P_i - O_i)^2}{\sum_{i=1}^{N} |P_i - \bar{O}| + |O_i - \bar{P}|)^2} \]  
\[ r = \frac{\sum_{i=1}^{N} (P_i - \bar{P})(O_i - \bar{O})}{\sqrt{\sum_{i=1}^{N} (P_i - \bar{P})^2 \sum_{i=1}^{N} (O_i - \bar{O})^2}} \]

where \( P_i \) and \( O_i \) are the simulated and observed variables, respectively. \( N \) is the total number of predictions. \( \bar{P} \) and \( \bar{O} \) denote the average of predictions and observations, respectively. IOA ranges from 0 to 1 theoretically, with 1 suggesting perfect agreement between predictions and observations.

3 Results and discussion

3.1 Observed increasing \( O_3 \) concentration and OC/EC ratio

Figure 3a shows the annual variation of measured mean concentrations of \( O_3 \), \( NO_2 \), \( SO_2 \), \( CO \), 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 \( NO_2 \), \( SO_2 \), \( CO \), and PM\(_{2.5}\) concentrations during recent years are observed since the implementation of APPCAP (Figure 3a). The \( O_3 \) concentration, however, has increased by about 30% during the same period. Such an \( O_3 \) increase indicates a
considerable enhancement of the AOC, considering the controlling role of O$_3$ in the AOC in the troposphere (Brasseur et al., 1999). The reason for the AOC or O$_3$ increase since 2013 still remains elusive. Li et al. (2018) have proposed that the O$_3$ increase in China since 2013 is associated with the decreased removal efficiency of HO$_x$ (OH + peroxy) on aerosol surfaces caused by the reduced aerosol concentrations since the implementation of APPCAP. However, further studies need to be conducted to evaluate the O$_3$ contribution of the photolysis change caused by the aerosol-radiation interaction and aerosol-cloud interaction induced by decreasing aerosols in China.

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 ratio has substantially increased during the 3 years (about 44%). There are two possible 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 changes in OC and EC emissions due to the implementation of APPCAP. The large variability in OC and EC concentrations in Figure 3b suggests considerable emission changes, although it is still difficult to evaluate exactly how much the emissions have been changed. Since SOA formation is closely associated with the abundance of oxidants (Li et al., 2011b; Robinson et al., 2007), OA in BTH is expected to be more oxygenated (add oxygen) and hence to increase in mass with enhanced AOC.

3.2 Model evaluation

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,
The model performs well in reproducing the observed diurnal cycles of the surface temperature and relative humidity at the 4 stations (Figure 4). The simulated temporal variations of temperature and relative humidity are in good agreement with the observations at the meteorological station in Tianjin. However, in the other 3 cities, the model generally cannot well reproduce the fairly low temperature and high relative humidity during nighttime. In general, the model replicates the low winds during 3-7 October in Beijing, Tianjin, and Baoding, but slightly overestimates the wind speed in Shijiazhuang, particularly in the 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 in Beijing. Overall, the model still generally captures the temporal variations of wind directions in the 4 cities.

### 3.2.2 PM\(_{2.5}\), O\(_3\), and NO\(_2\)

The spatial distributions of simulated and observed daily PM\(_{2.5}\) concentration during the period from 3 to 8 October 2015 are presented in Figure 6 along with wind fields. This haze 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 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 air pollutants from south to north, and the PM\(_{2.5}\) concentration in BTH rapidly increased. From 5 to 7 October, the southerly wind continued and the haze became persistently severe in BTH. Finally, a strong northerly wind cleaned up the haze within several hours on 8 October. The model reasonably reproduces the haze evolution in BTH, but it generally underestimates the PM\(_{2.5}\) concentration in Shandong province.

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
is remarkably enhanced during the maturation stage, ranging from 30 to 90 µg m$^{-3}$, which is
well predicted by the model. The MB, NMB, IOA, and $r$ for the simulated SOA concentration
are -2.1 µg m$^{-3}$, -6.9%, 0.89, and 0.81, respectively. Although the IOA and $r$ for the simulated
EC concentration reach 0.92 and 0.90, respectively, the model considerably underestimates
the EC concentration against measurement on October 6 and 7, which is likely caused by the
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.

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 O$_3$ (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.

3.3.1 OA component changes

Figures 10a and 10b show the variation of POA, SOA, and TOA concentrations as a
function of the O$_3$ and OH concentration changes over BTH by differentiating REF and the 4
sensitivity experiments, respectively. The SOA level decreases almost linearly with
decreasing O$_3$ or OH concentrations, indicating that the AOC plays an important role in the
SOA formation over BTH. In the SEN4 experiment with the most reduction of the AOC, the
SOA concentration in BTH is reduced by 31.3% or 5.2 µg m$^{-3}$ on average during the episode.
The reduction in POA level with decreasing O$_3$ and OH concentrations is generally not
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 \(O_3\) 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 radiation and thermodynamical profiles, through enhancing aerosol scattering and absorption 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 1.2 W m\(^{-2}\) on average in BTH, and the surface temperature is decreased by around 0.016 \(^\circ\)C during daytime. Effects of the AOC change on the temperature profile is not significant, and the daytime temperature decrease in the SEN3 experiment is less than 0.005 \(^\circ\)C within 1 km height from surface.

### 3.3.2 SOA spatial change in SEN3

Among the 4 experiments, the \(O_3\) change over BTH in SEN3 is close to the observed 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 distribution of SOA concentrations in BTH during the haze episode, Figure 11 shows the spatial distributions of the variation in the main oxidant (OH) and SOA concentrations averaged from 4 to 7 October by differentiating REF and the SEN3 experiment. When the 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 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
coemitted 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 O₃ 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
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.

Four sensitivity experiments with different reductions in the AOC show that changing AOC substantially affects the SOA formation. In the SEN4 scenario, characterized by a 30.9% (35.7%) decrease in O$_3$ (OH) concentration, the SOA concentration is reduced by 31.3% and the SOA mass fraction in TOA is reduced from 0.52 to 0.43. Spatially, the SOA reduction is 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 in the non-traditional SOA module, the largest SOA reduction in the reduced AOC environment occurs in the PSOA, followed by the ASOA and BSOA. By contrast, the SOA reduction in the HSOA is negligible.

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.

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,
analyzed the study data, validated the model performance, and reviewed the manuscript. Suixin Liu, Yang Qian, Yi Chen 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.

Acknowledgements. This work is financially supported by the National Key R&D Plan (Quantitative Relationship and Regulation Principle between Regional Oxidation Capacity of Atmospheric and Air Quality (2017YFC0210000)) and National Research Program for Key Issues in Air Pollution Control (DQGG0105). Tian Feng is supported by National Natural Science Foundation of China (no. 41703127, 41430424, 41661144020).
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Table I Anthropogenic emissions of various species in the simulation domain in October 2015 (Unit: Mton month⁻¹)

<table>
<thead>
<tr>
<th>Species</th>
<th>NOx</th>
<th>SO₂</th>
<th>NH₃</th>
<th>CO</th>
<th>VOC</th>
<th>OC</th>
<th>EC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Beijing</td>
<td>0.31</td>
<td>0.02</td>
<td>0.05</td>
<td>0.66</td>
<td>1.51</td>
<td>0.03</td>
<td>0.01</td>
</tr>
<tr>
<td>Tianjin</td>
<td>0.24</td>
<td>0.09</td>
<td>0.05</td>
<td>0.09</td>
<td>2.8</td>
<td>0.05</td>
<td>0.01</td>
</tr>
<tr>
<td>Hebei</td>
<td>2.21</td>
<td>0.7</td>
<td>0.62</td>
<td>3.59</td>
<td>21.59</td>
<td>0.41</td>
<td>0.06</td>
</tr>
<tr>
<td>Domain</td>
<td>14.21</td>
<td>7.1</td>
<td>4.45</td>
<td>22.19</td>
<td>124.71</td>
<td>2.56</td>
<td>0.3</td>
</tr>
</tbody>
</table>
### Table 2 WRF-Chem model configuration

<table>
<thead>
<tr>
<th>Item</th>
<th>Configuration</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Period</strong></td>
<td>3 ~ 8 October 2015</td>
</tr>
<tr>
<td><strong>Regions</strong></td>
<td>Beijing-Tianjin-Hebei, China</td>
</tr>
<tr>
<td><strong>Domain center</strong></td>
<td>116°E, 38°N</td>
</tr>
<tr>
<td><strong>Domain size</strong></td>
<td>1200 km × 1200 km</td>
</tr>
<tr>
<td><strong>Horizontal resolution</strong></td>
<td>6 km × 6 km</td>
</tr>
<tr>
<td><strong>Vertical resolution</strong></td>
<td>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</td>
</tr>
<tr>
<td><strong>Microphysics scheme</strong></td>
<td>WRF Single-Moment 6-class scheme (Hong and Lim, 2006)</td>
</tr>
<tr>
<td><strong>Boundary layer scheme</strong></td>
<td>MYJ TKE scheme (Janjić, 2002)</td>
</tr>
<tr>
<td><strong>Surface layer scheme</strong></td>
<td>MYJ surface scheme (Janjić, 2002)</td>
</tr>
<tr>
<td><strong>Land-surface scheme</strong></td>
<td>Noah land surface model (Chen and Dudhia, 2001)</td>
</tr>
<tr>
<td><strong>Longwave radiation scheme</strong></td>
<td>New Goddard scheme (Chou et al., 2001)</td>
</tr>
<tr>
<td><strong>Shortwave radiation scheme</strong></td>
<td>New Goddard scheme (Chou and Suarez, 1999)</td>
</tr>
<tr>
<td><strong>Meteorological boundary and initial condition</strong></td>
<td>NCEP 1° × 1° reanalysis data</td>
</tr>
<tr>
<td><strong>Chemical boundary and initial condition</strong></td>
<td>MOZART 6-h output (Horowitz et al., 2003)</td>
</tr>
<tr>
<td><strong>Anthropogenic emission inventory</strong></td>
<td>SAPRC99 chemical mechanism emissions (Zhang et al., 2009), base year: 2013</td>
</tr>
<tr>
<td><strong>Biogenic emission inventory</strong></td>
<td>MEGAN model developed by Guenther et al. (2006)</td>
</tr>
<tr>
<td><strong>Spin-up time</strong></td>
<td>1.5 days</td>
</tr>
</tbody>
</table>
Table 3 Description of the reference simulation and sensitivity experiments

<table>
<thead>
<tr>
<th>Case ID</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>REF</td>
<td>The reference simulation constrained by observations</td>
</tr>
<tr>
<td>SEN1</td>
<td>10% decrease in photolysis frequencies</td>
</tr>
<tr>
<td>SEN2</td>
<td>20% decrease in photolysis frequencies</td>
</tr>
<tr>
<td>SEN3</td>
<td>30% decrease in photolysis frequencies</td>
</tr>
<tr>
<td>SEN4</td>
<td>40% decrease in photolysis frequencies</td>
</tr>
</tbody>
</table>
Figure captions

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).
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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