Multiple pathways for the formation of secondary organic aerosol in North China Plain in summer

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Abstract

Secondary organic aerosol (SOA) has been identified as a major contributor to fine particulate matter (PM$_{2.5}$) in North China Plain (NCP). However, the chemical mechanisms involved are still unclear due to incomplete understanding of its multiple formation processes. Here we report field observations in summer in Handan of NCP, based on high-resolution online measurements. Our results reveal the formation of SOA via photochemistry and two types of aqueous-phase chemistry, the latter of which include nocturnal and daytime processing. The photochemical pathway is the most important under high O$_x$ (=$O_3$ + NO$_2$) conditions (65.1 ± 20.4 ppb). The efficient SOA formation from photochemistry (phochem-SOA) dominated the daytime (65% to OA) with an average growth rate of 0.8 μg m$^{-3}$ h$^{-1}$. During the high relative humidity (RH: 83.7 ± 12.5 %) period, strong nocturnal aqueous-phase SOA formation (aq-SOA) played a significant role in SOA production (45% to OA) with a nighttime growth rate of 0.6 μg m$^{-3}$ h$^{-1}$. Meanwhile, an equally fast growth rate of 0.6 μg m$^{-3}$ h$^{-1}$ of phochem-SOA from daytime aqueous-phase photochemistry was also observed, which contributed 39% to OA, showing that photochemistry in the aqueous phase is also a non-negligible pathway in summer. The primary-related-SOA (SOA attributed to primary particulate organics) and aq-SOA are related to residential coal combustion activities, supported by distinct fragments from polycyclic aromatic hydrocarbons (PAHs). Moreover, the conversion and rapidly oxidation of primary-related-SOA to aq-SOA could be possible in the aqueous phase under high-RH conditions. This work sheds light on the multiple formation pathways of SOA in ambient air of complex pollution, and improves our understanding of ambient SOA formation and aging in summer with high oxidation capacity.

KEYWORDS: secondary organic aerosol, aqueous-phase chemistry, photochemistry, multiple-phase chemistry, complex air pollution
1. Introduction

Rapid economic growth and urbanization processes have led to severe particulate air pollution in China, affecting air quality, climates and human health (Huang et al., 2014; Cohen et al., 2017; An et al., 2019). Organic aerosol (OA) is a major component of aerosol particles, consisting of 20-90% of fine particle mass (Jimenez et al., 2009; Zhang et al., 2011). OA is either emitted directly from primary sources (referred to as primary OA, POA) such as traffic, cooking, coal combustion, and biomass burning, or produced through gas-to-particle conversion (referred to as secondary OA, SOA) in the atmosphere. In recent years, with the implementation of control measures, the POA fraction is decreasing and SOA fraction is increasing in North China Plain (NCP), indicating that SOA is becoming more critical for urban air quality (Huang et al., 2019; Xu et al., 2019; Gu et al., 2020). However, our understanding of the formation mechanisms and evolution processes of SOA is still limited.

Generally, SOA can be formed through gas-phase photochemical oxidation of volatile organic compounds (VOCs) followed by nucleation or condensation of oxidation products onto the preexisting particles (Donahue et al., 2006). Herndon et al., (2008) showed that oxygenated organic aerosol (OOA), a surrogate of SOA, was well correlated with odd oxygen ($O_x = O_3 + NO_2$) during photochemical processing. SOA can also be formed in the aqueous phase on wet aerosols, clouds and fogs through further chemical processes of water-soluble organic compounds or organic products of gas-phase photochemistry (Ervens et al., 2011, 2014). A growing number of laboratory studies and field measurements have indicated that aqueous-phase processes contribute efficiently to the formation of SOA (Gilardoni et al., 2016; Bikkina et al., 2017). However, how photochemistry and aqueous-phase chemistry coordinate to affect the formation of SOA is still unclear, despite numerous measurements to explore this question using aerosol chemical speciation monitor (ACSM) or aerosol mass spectrometer (AMS) (Hu et al., 2016b; Hu et al., 2017; Sun et al., 2016; Li et al., 2017; Sun et al., 2018b; Huang et al., 2019; Gu et al., 2020; Kuang et al., 2020). Field measurements in Beijing suggested that gas-phase photochemical oxidation can play a dominant role in SOA formation (Sun et al., 2016; Hu et al., 2016a). Xu et al., (2017) showed that less oxidized-OOA (LO-OOA) was mainly formed through photochemical oxidation, while the more oxidized-OOA (MO-OOA) formation was dominantly formed by aqueous-phase chemistry in Beijing for different seasons. Kuang et al. (2020) investigated the effects of gas-phase and aqueous-phase photochemical processes on the formation of SOA and found that photochemical aqueous-phase SOA formation dominantly contributed to daytime OOA formation in winter Gucheng, located between Beijing (~100 km) and Baoding (~40 km) on the NCP. We found that photochemical processing attributed mostly to MO-OOA in summertime Beijing (Gu et al., 2020). Although these studies provided important insights into SOA formation processes, our understanding on the photochemical and aqueous-phase formation pathways for SOA and their
impacts on oxidation degree are far from complete. This lack of understanding is especially so under the conditions that atmospheric oxidative capacity and pollution characteristics have been largely changing in China due to large reduction in direct emissions of air pollutants.

In this study, we investigated the photochemical versus aqueous-phase processing for SOA composition and oxidation degree of OA in summertime Handan, which is a typical industrialized city in the NCP region. The city is located at the intersectional area of Hebei, Shanxi, Henan, and Shandong—four heavily urbanized and industrialized provinces (Fig. S1), and it is therefore an ideal site to investigate the SOA formation pathways in the NCP region. The multiple formation pathways, evolution of SOA composition, and oxidation degree under different meteorological conditions were discussed, which sheds light on the aqueous-phase chemistry and photochemical processing in SOA formation in the NCP region of China.

2. Experimental methods

2.1 Sampling site

Measurements were conducted from 10th August 2019 to 17th September 2019 on the campus of Hebei University of Engineering (36.57° N, 114.50° E), located at the southeast edge of urban Handan (Fig. S1). The site is surrounded by a school and residential areas, ~300 m north to South Ring Road and ~400 m northeast to the Handan Highway (S313). The sampling site is on the rooftop of a four-floor building, approximately 12 m above the ground.

2.2 Instrumentation

Real-time non-refractory PM$_{2.5}$ composition was measured by a soot particle long time-of-flight aerosol mass spectrometer (SP-LToF-AMS, Aerodyne Research Inc.) with a time resolution of 1 min. The detailed instrument description and operation of AMS were reported in Onasch et al., (2012). Compared to the conventional AMS, the LToF mass analyzer can provide much better mass resolution of ~8000. During the campaign, the instrument was operated in the “laser off” mode and only the standard tungsten vaporizer was applied. Therefore, only non-refractory PM$_{2.5}$ components (NR-PM$_{2.5}$) were measured, including organics (Org), nitrate (NO$_3$), sulfate (SO$_4$), ammonium (NH$_4$), and chloride (Chl). Ambient air was sampled and dried by a Nafion dryer (MD-700-24S, Perma Pure, Inc.) at a flow rate of 5 L min$^{-1}$, and then sub-sampled into the SP-LToF-AMS at a flow rate of ~0.1 L min$^{-1}$. An aerodynamic PM$_{2.5}$ lens was used to focus the particle into a beam, which was then impacted on the heated tungsten surface (~600 °C) and flash-vaporized. Electron ionization with 70 eV was used to ionize the vaporized gases. The ionization efficiency (IE) and the relative ionization efficiency (RIE) calibrations (Jimenez et al., 2003) were conducted by using 350 nm ammonium nitrate (NH$_4$NO$_3$) and ammonium sulfate ((NH$_4$)$_2$SO$_4$) particles.
Gaseous pollutants including SO$_2$ (9850 SO$_2$ analyzer, Ecotech), NO$_2$ (Model 42i NO-NO$_2$-NO$_x$ analyzer, Thermo Scientific), CO (Model 48i carbon monoxide analyzer, Thermo Scientific), O$_3$ (Model 49i ozone analyzer, Thermo Scientific), and meteorological parameters including RH and temperature were also measured during the observation period. Furthermore, an aethalometer (Model AE-33, Magee Scientific) was deployed to measure the mass concentration of black carbon (BC) at a time resolution of 1 min.

2.3 Data Analysis

The data analysis software (SQUIRREL, version 1.63I and PIKA, 1.23I) within Igor Pro 6.37 (WaveMetrics) was used to analyze the AMS data. The experimental RIE values of 4 (NH$_4$) and 1.2 (SO$_4$) and the standard RIE values of 1.4 (Org), 1.1 (NO$_3$) and 1.3 (Chl) were used.

The composition-dependent collection efficiency (CDCE, Middlebrook et al., 2012) was used to compensate for the incomplete detection caused by particle bounce on the vaporizer. An improved Ambient (I-A) method was adopted for the elemental ratio analysis of high-resolution (HR) OA mass spectra, such as oxygen-to-carbon (O:C), and hydrogen-to-carbon (H:C) ratios (Canagaratna et al., 2015), which reflect the relative composition and oxidation degree for different OA source. In our study, PMF was performed on HR mass spectra of OA for ions with $m/z$ values of 12-120, together with the signals from integer $m/z$ values between 121 to 300 (i.e., unit mass resolution, UMR) using SoFi (version 6.3) in Igor Pro (Paatero, 1999; Canonaco et al., 2013). The data and error matrices were preprocessed according to Elser et al., (2016) and detailed description of PMF analysis was given elsewhere (Canonaco et al. 2013; Elser et al. 2016). Unconstrained PMF solutions with varied factor numbers were analyzed and six factors were resolved, including two primary and four secondary organic factors (Fig. 3). The six-factor solution was preferred because the five-factor solution was not able to separate high signal of $m/z$ 44 (which represents high oxidation state) from primary organic aerosol (POA) factors, while the seven-factor solution added additional OOA factors with similar profiles and noisy time series for which no physical interpretation could be found. The two POA factors consisted of a traffic-related factor (hydrocarbon-like OA, HOA) and a cooking-related factor (COA), which had been resolved in previous summer studies in NCP (Elser et al., 2016; Hu et al., 2016b; Sun et al., 2016; Huang et al., 2019). AMS source apportionment studies often report one or two oxygenated organic aerosol (OOA) factors that are distinguished by the extent of oxygcnation and linked to volatility or oxidation degree. Owing to higher mass resolution of LTOF-AMS and the inclusion of integer-mass signals for $m/z$ from 121 to 300 for high-molecular-weight species such as polycyclic aromatic hydrocarbons (PAHs), we herein resolved four SOA factors. These four SOA factors include aq-SOA attributable to aqueous-phase chemistry, photochem-SOA attributable to photochemistry, primary-related-SOA attributable to prompt oxidation of POA during emission, and fresh-SOA with a lower $f_{44}/f_{43}$ ratio (fraction of $m/z$ 44 and 43 in OA).
The aerosol liquid water content (ALWC) was simulated by ISORROPIA-II model (Fountoukis and Nenes, 2007; Hennigan et al., 2015) using the measurements of ambient inorganic species (NO3, SO4, NH4, and Chl) and meteorological parameters (temperature and RH). The simulation was run in “metastable” mode where all components are assumed to be deliquescent and contain no solid matter. The concentrations and speciation (if dissociated) of those inorganic species in thermodynamic equilibrium was then simulated by the model and then the ALWC was calculated. The ISORROPIA-II model does not consider the contribution to ALWC from organics, since inorganic aerosols dominate the water uptake by ambient particles with a contribution of approximate >80% of the total ALWC (Huang et al., 2020).

3. Results and discussion

3.1 SOA sources

In our study, SOA accounted for 69% (13.5 μg m\(^{-3}\)) of the total OA (19.6 μg m\(^{-3}\)), representing the dominant fraction in OA in summer Handan. Among the four PMF-resolved SOA sources (Fig. 1), phochem-SOA dominated (31% to total OA), followed by fresh-SOA (18%), aq-SOA (15%), and primary-related-SOA (5%). Since we focus on SOA formation in this study, detailed descriptions of the HOA (12%) and COA (19%) is provided in section 1.1 in the SI. The mass spectral profiles of the six OA source factors are shown in Fig. 1, while the time series of the SOA factors are shown in Fig. 2. In particular, a remarkable continuous growth of aq-SOA concentration (from ~0.3 μg m\(^{-3}\) to 25.2 μg m\(^{-3}\)) and ALWC (from 3.1 μg m\(^{-3}\) to 486.1 μg m\(^{-3}\)) occurred on 24\(^{th}\)-28\(^{th}\) August (Fig. 2d). Meanwhile, the O:C ratio indicative of OA oxidation state displayed a continuous increase from 0.52 to a maximum of 0.93 during this time (Fig. 2e), consistent with the continuous increase in RH (reaching over 95%). This observation hints that during this period aqueous-phase processing might have played an important role in aq-SOA formation. This role of aqueous-phase processing in SOA formation is not just specific to this particular event, but also important in the whole campaign, which is discussed in detail in section 3.3 later.

To further investigate the SOA formation mechanism, the dataset was segregated into three periods according to different features depends on meteorological parameters (Fig. 2), i.e., the reference period (P1), high-O\(_x\) period (P2) and high-RH period (P3). Briefly, the reference period, P1, was characterized by a low average OA concentration (15.4 ± 3.2 μg m\(^{-3}\)) and was mainly affected by clean air from southwest of the sampling site and precipitation activities (Table S1). The high-O\(_x\) period (P2) was featured by a high O\(_x\) concentration (65.1 ± 20.4 ppb), warmer temperatures (26.4 ± 4.0 °C) but lower RH (57.7 ± 17.5 %). The mass loadings of OA (19.8 ± 4.7 μg m\(^{-3}\)) and other pollutants in P2 were higher than those in P1 (Table S1). P3 was
assigned as a high-RH period because of the noticeably high RH (83.7 ± 12.5 %) and high ALWC (95.4 ± 114.2 μg m$^{-3}$). Winds were weak (<1.0 m s$^{-1}$) throughout this period, indicative of stagnant conditions, which facilitated pollutant accumulation and resulted in the highest average OA concentrations (25.0 ± 6.2 μg m$^{-3}$).

During the reference period (P1), SOA had the lowest contribution to OA (57%), and the phochem-SOA and aq-SOA constituted 22% and 21% to total OA, respectively. For the high-Ox period (P2), enhanced SOA formation was found, with the SOA fraction increased to 71% of the total OA. The phochem-SOA showed the highest mass loading of 7.3 μg m$^{-3}$ and highest contribution of 37% to total OA. These increases suggest that high-Ox condition facilitates the production of SOA by photochemistry, making the phochem-SOA the major source of SOA during P2. During the high-RH period (P3), SOA fraction continually increased, approaching 79% in total OA, and the SOA was mainly contributed by aq-SOA and fresh-SOA. The mass contribution of aq-SOA increased dramatically from 9% to total OA during P2 to 33% during P3 (Fig. S2), and average mass concentrations from 1.8 μg m$^{-3}$ to 8.3 μg m$^{-3}$, which suggests rapid SOA production through the aqueous-phase chemistry. Comparatively, the contribution of fresh-SOA was about ~20% in both P2 and P3, but lower in P1 (9%), suggesting that the formation fresh-SOA was effected by both high Ox and high RH. It should also be noted that O:C ratio increased in the succession from P1 (0.73) to P2 (0.74) and further to P3 (0.77), accompanied by continually decrease of H:C ratio from 1.64 to 1.56, and to 1.53 (Fig. 3), suggesting the increase of OA oxidation degree. As a result, the high Ox, in P2 and high RH in P3 (as compared to P1) promoted the formation of SOA, specifically phochem-SOA (in P2) and aq-SOA (in P3), leading to the increase in the degree of oxygenation in total OA.

Although the primary-related-SOA constituted a small fraction and showed little variation during P1−P3 (3%~5%), this SOA source is also of particular interest because of its distinctive fragments with high m/z values in the mass spectrum (Fig. 1d). At m/z < 120, the primary-related-SOA had higher intensities for m/z 43 (mainly C$_2$H$_4$O$^+$) and m/z 44 (mainly CO$_2$) than those in POA, indicating a typical nature of less-oxidized SOA. At m/z > 120, PAH-derived fragments are clearly evident in the mass spectrum of the primary-related-SOA, as indicated by PAH-like ions at m/z 152, 165, 178, 189, 202, 216, 226 + 228, 240 + 242, 250 + 252, 264 + 266, and 276 + 278 (Dzepina et al., 2007). Previous AMS studies have observed pronounced peaks of PAH ions in POA mass spectra, such as those in coal combustion organic aerosol (CCOA) and biomass burning organic aerosol (BBOA) (Hu et al., 2016b; Zhao et al., 2019), but rarely in SOA. This observation implies that the primary-related-SOA may be related to the POA originated from domestic coal combustion (Xu et al., 2006). Moreover, this SOA factor exhibited relatively better correlations with some gaseous pollutants (Fig. S4), such as CO ($R^2 = 0.6$) and NO$_2$ ($R = 0.5$), and also tracked with HOA ($R = 0.4$). These observations suggest that the primary-related-SOA might be transformed from locally emitted POA as a non-
negligible source to SOA. Overall, our results suggest that SOA could be formed through different pathways, in particular photochemistry, aqueous-phase chemistry, and conversion of POA to SOA contributed to SOA formation.

3.2 Photochemistry

As expected for summertime, photochemistry associated with $O_x$ has significant impacts on the formation and evolution of SOA. Herein, the relationships between OA factors and $O_x$ were investigated to offer insights into the formation mechanisms of SOA associated with the ozone production chemistry (Herndon et al., 2008). During P2, as $O_x$ increased, the mass loadings of phochem-SOA showed a substantially increasing trend when $O_x$ was > 30 ppb and eventually saturated when $O_x$ was > 100 ppb, raising the contribution of phochem-SOA from 20% to 61% of total OA (Fig. 4). This observation indicates the importance of photochemistry in the formation of phochem-SOA in summer, in which high $O_x$ concentration as well as temperature corresponding to strong atmospheric oxidative capacity, can accelerate the photochemical formation (Duan et al., 2021). As a comparison, the mass concentrations of other OA factors except phochem-SOA showed decreasing trends as $O_x$ increased (Fig. 4c). Such differences between SOA factors are likely due to the enhanced secondary production/transformation from POA and fresher SOA factors to the more aged phochem-SOA. Note that the O:C ratio presented a faster increasing rate as a function of $O_x$ (from 0.6 to 1.0, Fig. 4d) than those in P1 and P3, suggesting that photochemistry resulted in higher OA oxidation state during P2.

The average diurnal variations of SOA factors, O:C ratios, $O_x$, temperature, and RH during different periods are shown in Fig. 6 and Fig. S7. During P2, phochem-SOA was produced quickly and played the dominant role during daytime, while its concentration typically decreased during nighttime. The average concentration of phochem-SOA increased continually from 4.3 $\mu$g m$^{-3}$ at 6:00 local time (LT) to 10.4 $\mu$g m$^{-3}$ at 14:00 LT in 8 h, with the maximum phochem-SOA mass fraction in OA reaching 65% at 14:00 LT (Fig. 6c). This high average growth rate of 0.8 $\mu$g m$^{-3}$ h$^{-1}$ in phochem-SOA corresponded to the high $O_x$ concentration, high temperature and strong solar radiation in daytime (Fig. S7). In comparison, the concentrations and the contributions of other SOA factors deceased continuously from 6:00 to 14:00 LT (Fig. 6c). This result further supports the idea that during the high-$O_x$ period of summer, photochemistry has significant impacts on SOA formation, especially on phochem-SOA. Note that the role of photochemistry in the formation of phochem-SOA is not limited to the gas-phase photochemistry, but the photochemistry can also occur in the aqueous phase (Kuang et al., 2020). This is the case for P3 in our study, which is discussed further in section 3.3 below. In addition, the potential transformation from POA factors and fresh SOA factors to phochem-
SOA through photochemical oxidation could also noticeably affect OA characteristics such as oxidation state in summer daytime.

3.3 Aqueous-phase chemistry

The aqueous-phase chemistry has imposed significant impacts on SOA formation during this field campaign. To further explore the formation mechanism of SOA associated with aqueous-phase chemistry, the relationships between different OA factors and ALWC were investigated. During P3, the mass concentration of aq-SOA increased from 5 µg m\(^{-3}\) to 17 µg m\(^{-3}\), yet its fraction showed a particularly pronounced rise from 22.5% to 52% of total OA when ALWC increased from 0.3 to 200 µg m\(^{-3}\) (Fig. 5e and f). Note that the strong correlation between aq-SOA and ALWC was not only observed in P3. Rather, the time series of aq-SOA and ALWC were remarkably well correlated throughout the entire campaign (\(R=0.7\), Fig. S4). This general correlation further confirms the important role of aqueous-phase chemistry in the formation of aq-SOA and characterized the aqueous-phase formation of aq-SOA throughout the campaign rather than only in the high-RH event as shown in section 3.1 earlier. We also found that the concentration and fraction of aq-SOA became stable when ALWC was > 200 µg m\(^{-3}\), which is probably attributable to that the aq-SOA formation within droplets was soon outweighed by the scavenging processes when RH was high enough (> 95%). Fig. 5e shows that the fresh-SOA has similar increasing trend with aq-SOA as ALWC increased, which suggests that aqueous-phase chemistry might have also played an important role in the formation of fresh-SOA. The fresh-SOA also increased slightly as O\(_x\) increased (Fig. 4e), suggesting that both the aqueous-phase chemistry and the photochemistry (including that in the aqueous phase) participated to produce fresh-SOA simultaneously.

The O:C ratio shows an obvious increase from 0.7 to around 0.85 when ALWC increases to 200 µg m\(^{-3}\), after which it remains relatively stable (0.85) as the ALWC increases further (Fig. 5). These results suggest that aqueous-phase chemistry can affect the oxidation degree of OA by changing SOA composition, especially the enhanced contribution of aq-SOA. However, the growth rate of O:C ratios as ALWC increases in P3 was lower than that in P2 (up to 1 as O\(_x\) increases). Also, the correlation between O:C vs. O\(_x\) in P2 (\(R=0.6\)) was stronger than O:C vs. ALWC (\(R=0.3\)) (Fig. S8). This result illustrates that photochemistry is more efficient in elevating the oxidation degree of OA than is the aqueous-phase chemistry.

Fig. 6e and Fig. 6f illustrate the different types of aqueous-phase chemistry in daytime and nighttime. The aq-SOA shows a quite clear and unique diurnal pattern in P3, with much higher mass concentration during the whole day (especially at nighttime) than those in P1 and P2. This may be attributed to the stagnant meteorological conditions and high RH (thus ALWC), which facilitated the continuous formation of aq-SOA in P3. During the daytime, the mass
concentration of aq-SOA decreased from 6:00 to 16:00 LT, consistent with the decrease of RH and the increase of temperature (Fig. S7). After 16:00 LT, aq-SOA started to increase from 4.7 $\mu$g m$^{-3}$ to 12.7 $\mu$g m$^{-3}$ at 6:00 LT, which showed a rapid nighttime growth rate of 0.6 $\mu$g m$^{-3}$ h$^{-1}$. Higher RH (thus ALWC) and lower temperature were found at nighttime of P3. This likely indicates that the dark aqueous-phase SOA formation under high-RH conditions was strong enough to counteract the nighttime scavenging processes. Therefore, the dark aqueous-phase chemistry forming aq-SOA shows a dominant role (over 40% to OA) during nighttime under high-RH conditions (P3).

In addition, we also noticed that significant phochem-SOA formation also occurred during daytime in P3 when RH and ALWC were high, with an average growth rate of 0.6 $\mu$g m$^{-3}$ h$^{-1}$. This observation is similar to results in a previous study showing that both aqueous-phase and gas-phase photochemical reactions substantially contributed to the formation of OOA (a surrogate of SOA) during the high-RH period (Kuang et al., 2020). The rapid daytime phochem-SOA formation in our study probably occurred in the aqueous phase driven by photochemical reactions during daytime under humid conditions with high ALWC. Under such high-RH level (RH > 80%), the water-soluble species produced from photochemistry in the gas phase can also partition into the aqueous phase and be further oxidized to form low-volatility products (Carlton et al., 2007; Sullivan et al., 2016). Previous studies have demonstrated that gas-phase oxidants such as OH radicals and H$_2$O$_2$ can also partition to the aqueous phase to further oxidize dissolved the oxidized VOCs (OVOCs) into aq-SOA (Ye et al., 2018). Other studies also suggested that photochemical reactions in the aqueous droplets can occur through direct photolysis or through oxidation by oxidants (Ervens et al., 2011; 2014; Ye et al., 2018). Therefore, in our campaign, dark aqueous-phase chemistry played significant roles in rapid aq-SOA formation during nighttime, while the aqueous-phase photochemistry during daytime might be responsible for rapid daytime phochem-SOA formation under high-RH conditions such as during P3. This comparison demonstrates that the nocturnal aqueous-phase chemistry and daytime aqueous-phase photochemistry were both important pathways in the total SOA growth.

It is worth noting that three peaks were found in the diurnal variation of fresh-SOA in P3. The peaks at around 6:00 and 19:00 LT were similar to those of aq-SOA, while the peak at around 13:00 LT corresponded to the peak in the diurnal cycle of O$_5$ (Fig. 6e). This three-peak diurnal pattern hints that both the dark aqueous-phase chemistry and the daytime photochemistry (either in the gas phase or in the aqueous phase) are important in the formation of fresh-SOA. Our analysis on formation pathways of these SOA factors suggest the potential interactive roles of gas-phase oxidation, gas-particle partitioning, and aqueous-phase oxidation in the formation of SOA.
3.4 SOA from POA transformation

The photochemistry and aqueous-phase chemistry show distinct effects on POA evolution and SOA formation. The relationships between phochem-SOA/aq-SOA and other POA-related components (HOA + COA + primary-related-SOA) were plotted in Fig. 7. A strong negative correlation ($R=-0.8$) between POA-related components and phochem-SOA was observed (Fig. 7c), consistent with the decrease in mass concentration of POA-related components during P2. This observation suggests that the production of phochem-SOA was at least partly facilitated by photochemical transformation of other OA components. In addition, compared with P1 and P3, a more positive promotion on the phochem-SOA formation was observed in P2 when $O_3$ was more than 40 ppb. These observations confirm the results in section 3.2 that intensive formation of phochem-SOA was not only produced by photochemical oxidation from VOCs at high-$O_3$ levels, but also potentially through the transformation of POA-related components into phochem-SOA.

In comparison, POA-related components and aq-SOA correlate weakly (Fig. 7b). When ALWC ($<20 \mu g \cdot m^{-3}$) and nitrate concentrations were lower ($<3 \mu g \cdot m^{-3}$), mostly during P1 and P2, POA-related components and aq-SOA showed almost no correlation ($R=0.1$). However, when ALWC concentration and nitrate concentration were higher than those thresholds above (data points with yellow/red colors mostly during P3), they had a relatively good negative correlation ($R= -0.5$), indicating the importance of ALWC and nitrate in aqueous-phase chemistry. This is consistent with results in winter Beijing (Wang et al., 2021), where POA factor had strong negative correlations with aq-SOA, suggesting that these POA factors might produce aq-SOA by aqueous-phase oxidation. In addition, under high-ALWC conditions, nitrate had similar formation mechanisms with aq-SOA or high nitrate supports the potential formation/transformation from POA-related components to aq-SOA, which is consistent with the results in section 3.3. The phenomenon of negative correlation between POA-related components and SOA at high $O_3$/ALWC further emphasizes the importance of conversion from POA to SOA.

As shown in the van Krevelen (VK) plot (Fig. 8a), O:C and H:C both increase in the succession from primary-related-SOA to phochem-SOA and eventually to aq-SOA, supporting a successive oxidation sequence from primary-related-SOA to aq-SOA. Generally, H:C shows a decreasing trend as O:C increases for organic compounds during oxidation in other studies (Ng et al., 2011; Gilardoni et al., 2016; Lee et al., 2017; Zhao et al., 2019; Chen et al., 2021), suggesting a general negative correlation between H:C and O:C. This positive relationship of O:C and H:C evolution during oxidative aging in this study is interesting. It might be caused by ring-breaking reactions which could further promote the transformation of aromatic POA to aq-SOA. Previous studies in both laboratory (Huang et al., 2018; Wang et al., 2020) and field...
(Hu et al., 2016a) demonstrated that the OH-initiated ring-breaking reactions of aromatic species can occur in the aqueous phase and form highly oxidized oxygenated compounds. For example, Hems and Abbatt (2018) suggested that nitrophenol molecules could react rapidly with OH radicals in aqueous solutions with the addition of OH functional groups to the aromatic ring at the initial stage, followed by fragmentation to multifunctional organic species with high H:C and O:C ratios. Wang et al. (2021) found that the ring-breaking oxidation of aromatic FF-POA was the mechanism for aq-SOA formation. Similar to those in primary-related-SOA, PAH-like ions was also found in the mass spectrum of aq-SOA at m/z > 150, albeit less pronounced, consistent with a previous study in Beijing (Wang et al., 2021). This is likely due to the oxidation of PAHs in the conversion of primary-related-SOA and aq-SOA, which is caused by enhanced hydroxylation of the aromatic ring and increased yields of carboxylic acids in OH-initiated reactions (Sun et al., 2010). This kind of ring-breaking oxidation of aromatic POA could thus lead to aq-SOA formation (Huang et al., 2018; Wang et al., 2021).

In addition, the locations of aq-SOA and the slope of overall OA are near the line with the slope of -1 in the VK plot, indicating more carboxylic acid formation while the replacement of a hydrogen atom with a carboxylic acid group (–COOH) (Heald et al., 2010; Ng et al., 2011). This observation supports that oxidation of PAHs was probably involved in the conversion of primary-related-SOA to aq-SOA through aqueous-phase chemistry, leading to functionalization as carbonyls and carboxylic acids.

4. Conclusion

The sources and formation mechanisms of SOA were investigated by online aerosol mass spectrometry and statistical (PMF) analysis from August to September of 2019 in Handan, a mid-sized industrialized city in NCP of China. Four specific SOA factors were resolved, including aq-SOA (15% to total OA), phochem-SOA (31%), fresh-SOA (18%) and primary-related-SOA (5%). By studying the formation of these SOA factors in different selected periods (P1-P3) against O₃ and ALWC, we found multiple pathways leading to their formation, sometimes with mixed pathways for one type of SOA.

Both photochemistry and aqueous-phase chemistry resulted in enhanced OA oxidation state, but the effect of photochemistry was stronger in SOA formation. During high-O₃ period, photochemistry had imposed significant impacts on the formation and evolution of SOA in summertime. The phochem-SOA contributed up to 65% to total OA in the daytime, with a high average growth rate of 0.8 μg m⁻³ h⁻¹, suggesting the efficient daytime formation of SOA from photochemistry. Rapid increases of the concentration and contribution (up to 61%) of phochem-SOA were found as O₃ increased, while all the other OA factors showed decreasing trends with O₃ concentration increasing. The difference suggests enhanced secondary transformation from
POA/fresh SOA factors to the more aged phochem-SOA under high-O\textsubscript{x} condition. However, during the high-RH period, two types of aqueous-phase chemistry were both important pathways for the SOA growth. During nighttime and under high-RH conditions, dark aqueous-phase chemistry played significant roles with rapid aq-SOA formation (up to 45% in total OA), while the aqueous-phase photochemistry was more important by rapid phochem-SOA formation during daytime (up to 39% in total OA). The primary-related-SOA was evidently linked to the POA originated from coal combustion activities, as indicated by the PAH-like ion peaks. Although it constituted a small fraction of 5%, the potential transformation and conversion from primary-related-SOA to aq-SOA could also be an important pathway via hydroxylation of the aromatic ring or ring-breaking oxidation of aromatic POA species through aqueous-phase chemistry. This study highlights the multiple reaction pathways, on top of multiple precursor types, on the SOA formation in industrialized regions, and calls form more in-depth study on the interactive roles of those formation pathways.

Data availability. Raw data used in this study are archived at the Institute of Earth Environment, Chinese Academy of Sciences, and are available on request by contacting the corresponding author.

Supplement. The Supplement related to this article is available online.

Competing interests. The authors declare that they have no conflict of interest.

Author contributions. RJH designed the study. Data analysis and source apportionment were done by YFG and RJH. YFG and RJH wrote the manuscript. YFG and RJH interpreted data and prepared display items. All authors commented on and discussed the manuscript.

Acknowledgement

This work was supported by the National Natural Science Foundation of China (no. 41925015), the Key Research Program of Frontier Sciences from the Chinese Academy of Sciences (no. ZDBS-LY-DQC001), the Strategic Priority Research Program of the Chinese Academy of Sciences (no. XDB40000000), and SKLLQG (no. SKLLQGTD1801).
References


https://doi.org/10.1021/acs.est.0c00526


https://doi.org/10.1002/9780470944479.ch11


**Figures**

**Fig. 1** HR and UMR mass spectra of OA factors: (a) HOA; (b) COA; (c) fresh-SOA; (d) primary-related-SOA; (e) phochem-SOA; (f) aq-SOA. Mass spectra signals less than 120 amu are colored by nine ion categories, signals equal to or greater than 120 amu are in unit mass resolution, and polycyclic aromatic hydrocarbons (PAHs) signals are in red on the right panels.
Fig. 2 Time series of (a) relative humidity (RH) and wind speed (WS), (b) O$_x$ and phochem-SOA, (c) fresh-SOA, aq-SOA and ALWC, (d) primary-related-SOA, (e) the O:C ratio and H:C ratio. The time series were categorized to be three typical periods based on total SOA mass concentrations and meteorology conditions: reference period (P1), high O$_x$ period (P2) and high RH period (P3).
Fig.3 Van Krevelen plot for OA of urban and suburban sites in China and other nations. Data points are colored by RH (%). P1, P2 and P3 in red circles represents the different periods in this study. All the data and related references can be found in Table S3.

Fig. 4 The mass concentration and contribution of OA factors as functions of O₃ in reference period (P1: a & b), high O₃ period (P2: c & d) and high RH period (P3: e & f) during this campaign. The yellow curves represent the O:C ration vs. O₃.
**Fig. 5** The mass concentration and contribution of OA factors as functions of ALWC in reference period (P1: a & b), high O₃ period (P2: c & d) and high RH period (P3: e & f) during this campaign. The yellow curves represent the O:C ration v.s. ALWC.

**Fig. 6** Diurnal patterns of mass concentration and mass contribution of OA factors in reference period (P1: a & b), high O₃ period (P2: c & d) and high RH period (P3: e & f). The growth rates of phochem-SOA in P2 and P3 are marked in (d) and (f). The growth rate of aq-SOA in P3 is marked in (e).
Fig. 7 Relationship between phochem-SOA and the sum of POA and primary-related-SOA colored by O\textsubscript{x} (ppb) in reference period (P1: a), high O\textsubscript{x} period (P2: c) and high RH period (P3: e); Relationship between aq-SOA and the sum of POA and primary-related-SOA colored by ALWC (μg m\textsuperscript{-3}) and sized by NO\textsubscript{3} (μg m\textsuperscript{-3}) in reference period (P1: b), high O\textsubscript{x} period (P2: d) and high RH period (P3: f) during this campaign.

Fig. 8 (a) Van Krevelen diagram for the O:C and H:C ratios of different OA factors (marked with squares) and bulk of OA during summer (marked with plus signs and colored by O\textsubscript{sc} carbon oxidation state (OSc)); (b) Triangle plot of f\textsubscript{44} versus f\textsubscript{43}, the dash lines were adopted from Ng et al. (2010) (marked with plus signs and colored by f\textsubscript{29}).