**Supplementary Information**

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

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**Table S1.** Summary of Mass Concentrations of $PM_{2.5}$ Species and OA Components ($\mu g\ m^{-3}$), Mixing Ratios of gas-phase pollutants, and meteorological parameters in the Summer Studies in Handan.

| | Handan Summer | | | |
|---|---|---|---|---|
| | All | P1 | P2 | P3 |
| Total | 37.3±19.0 | 29.3±12.7 | 36.0±14.7 | 64.1±29.4 |
| OA | 19.6±5.5 | 15.4±3.2 | 19.8±4.7 | 25.0±6.2 |
| HOA | 2.4±2.1 | 2.2±1.5 | 2.6±2.5 | 1.7±1.1 |
| COA | 3.7±2.6 | 4.6±3.3 | 3.1±2.2 | 3.4±2.8 |
| primary-SOA | 1.0±1.2 | 1.0±1.3 | 1.0±1.2 | 0.7±1.4 |
| fresh-SOA | 3.5±2.5 | 3.5±1.3 | 4.0±2.3 | 5.5±2.7 |
| phochem-SOA | 6.1±3.3 | 6.1±1.9 | 7.3±3.1 | 5.4±2.4 |
| aq-SOA | 3.9±3.5 | 2.9±2.2 | 1.8±2.0 | 8.3±6.3 |
| Sulfate | 7.2±4.9 | 5.9±5.8 | 7.1±4.0 | 11.8±6.2 |
| Nitrate | 4.3±6.3 | 3.5±2.9 | 3.0±4.4 | 14.9±11.3 |
| Ammonium | 2.7±2.5 | 2.2±1.9 | 2.4±1.7 | 6.5±4.1 |
| Chloride | 0.4±0.6 | 0.3±0.3 | 0.4±0.6 | 1.0±1.1 |
| BC | 3.1±2.0 | 2.0±1.2 | 3.3±1.9 | 4.9±2.4 |
| CO(ppm) | 0.8±0.7 | 0.6±0.6 | 0.8±0.8 | 1.3±0.5 |
| $NO_2$(ppb) | 14.4±9.9 | 11.8±5.3 | 15.6±11.7 | 15.9±5.4 |
| $SO_2$(ppb) | 4.0±4.6 | 2.4±2.5 | 5.2±5.5 | 2.2±1.5 |
| $O_3$(ppb) | 54.0±22.8 | 24.0±14.5 | 49.5±29.1 | 32.2±24.6 |
| WS(m/s) | 1.5±1.0 | 1.7±1.1 | 1.6±1.0 | 1.0±0.6 |
| WD(°) | 187.1±121.8 | 223.1±126.6 | 168.2±111.5 | 201.9±124.4 |
| T(℃) | 25.0±4.3 | 22.3±2.8 | 26.4±4.0 | 23.1±2.6 |
| RH(%) | 66.3±19.4 | 79.4±13.0 | 57.7±17.5 | 83.7±12.5 |
| ALWC | 21.4±51.3 | 22.6±48.0 | 8.4±15.8 | 95.4±114.2 |

**Table S2.** Concentrations of the main chemical components in $PM_1$/$PM_{2.5}$ during summer and winter observations in NCP in recent years.

| Sites | OA | SO4 | NO3 | NH4 | Cl | BC | PM | $PM_1$ | NR-$PM_1$ | $PM_{2.5}$ |
|---|---|---|---|---|---|---|---|---|---|---|
| Our study | 19.0 | 7.2 | 4.3 | 2.7 | 0.4 | 3.1 | | | | 36.7 |
| 2013 Summer, Handan (Zhao et al., 2019) | | 16.1 | 16.5 | 7.3 | 3.3 | | | | | 95.6 |
| 2017 Summer, Handan (Zhao et al., 2019) | | 13.4 | 5.0 | 6.2 | 0.7 | | | | | 64.8 |
| 2015 winter, Handan (Li et al., 2017) | 81.2 | 28.1 | 26.1 | 21.4 | 16.6 | 9.4 | | 187.6 | 173.4 | |
| 2018 Summer, Beijing (Xu et al., 2019b) | 12.7 | 6.5 | 7.4 | 4.3 | 0.2 | | | | 31.1 | |
| 2018 Summer, Beijing (Chen et al., 2020) | 12.2 | 3.9 | 2.5 | 2.2 | 0.1 | 3.2 | | 24.1 | | |
| 2019 Summer, Beijing (Chen et al., 2020) | 9.3 | 4.5 | 2.8 | 2.5 | 0.2 | | | 19.3 | | |
| 2019 Summer, Xian (Duan et al., 2020) | 14.0 | 3.9 | 2.8 | 1.7 | 0.1 | | | | | 22.5 |

**Table S3.** Elemental ratios and OM:OC ratios in OA obtained from field observations at urban and rural/suburban sites. The ratios are corrected by the "improved-ambient" method (Canagaratna et al., 2015).

| sites | site types | seasons | H:C | O:C | OM:OC | ref |
|---|---|---|---|---|---|---|
| our study | urban | summer 2019 | 1.58 | 0.75 | 2.17 | |
| | suburban | summer 2018 | 1.67 | 0.54 | 1.89 | Chen et al.2020b |
| Beijing | urban | summer 2012 | 1.63 | 0.53 | 1.88 | Hu et al.2017 |
| | | winter 2013 | 1.52 | 0.47 | 1.79 | |
| | | summer 2011 | 1.61 | 0.56 | 1.91 | Hu et al.2016a |
| | | winter 2010 | 1.65 | 0.32 | 1.58 | |
| Xi'An | urban | summer 2019 | 1.64 | 0.58 | 1.96 | Duan et al. 2020 |
| Hangzhou | urban | Before G20 | 1.78 | 0.39 | 1.69 | Li et al., 2017 |
| | | During G20 | 1.65 | 0.58 | 2.03 | |
| | | After G20 | 1.69 | 0.51 | 1.84 | |
| Lanzhou | urban | winter 2014 | 1.55 | 0.28 | 1.51 | Xu et al., 2016 |
| | | summer 2012 | 1.49 | 0.33 | 1.58 | |
| Guangzhou | suburban | winter 2014 Nov. | 1.63 | 0.53 | 1.87 | Qin et al., 2017 |
| | | winter 2014 Dec. | 1.65 | 0.53 | 1.87 | |
| Kaiping | suburban | autumn 2008 | 1.64 | 0.6 | 1.94 | Huang et al.,2011 |
| Heshan | suburban | autumn 2010 | 1.65 | 0.51 | 1.83 | Gong et al., 2012 |
| Shenzhen | urban | winter 2009 | 1.83 | 0.39 | 1.71 | He et al.,2011 |
| | | summer 2011 | 1.74 | 0.45 | 1.81 | Gong et al., 2012 |
| Shanghai | urban | summer 2010 | 1.92 | 0.4 | 1.69 | Huang et al.,2012 |
| Ziyang | suburban | winter 2013 | 1.56 | 0.65 | 2.02 | Hu et al.2016b |
| Jiaxing | suburban | summer 2010 | 1.94 | 0.36 | 1.67 | Huang et al.,2013 |
| | | winter 2010 | 1.73 | 0.43 | 1.75 | |
| HKUST | suburban | summer 2011 | 1.48 | 0.64 | 1.93 | Li et al., 2015 |
| | | winter 2012 | 1.53 | 0.53 | 1.8 | |
| MongKoK | urban | summer 2013 | 1.83 | 0.26 | 1.5 | lee et al., 2015 |
| Fresno.CA (US) | urban | winter 2010 | 1.75 | 0.35 | 1.63 | Ge et al. (2012) |
| Riverside,CA (US) | urban | summer 2005 | 1.71 | 0.44 | 1.73 | Docherty et al. (2011) |
| Korea | urban | winter 2019 | 1.79 | 0.37 | 1.67 | Kim et al. 2017 |
| Oregon (US) | No BB | summer 2013 | 1.48 | 0.84 | 2.26 | Zhou et al., 2017 |
| | BB infl | | 1.49 | 0.77 | 2.16 | |
| | BB plm | | 1.53 | 0.69 | 2.06 | |


**Fig. S1** Location of the $PM_{2.5}$ sampling site in Handan (the red star). The base map image was derived from AutoNavi Maps (Image © 2022 AutoNavi-GS).

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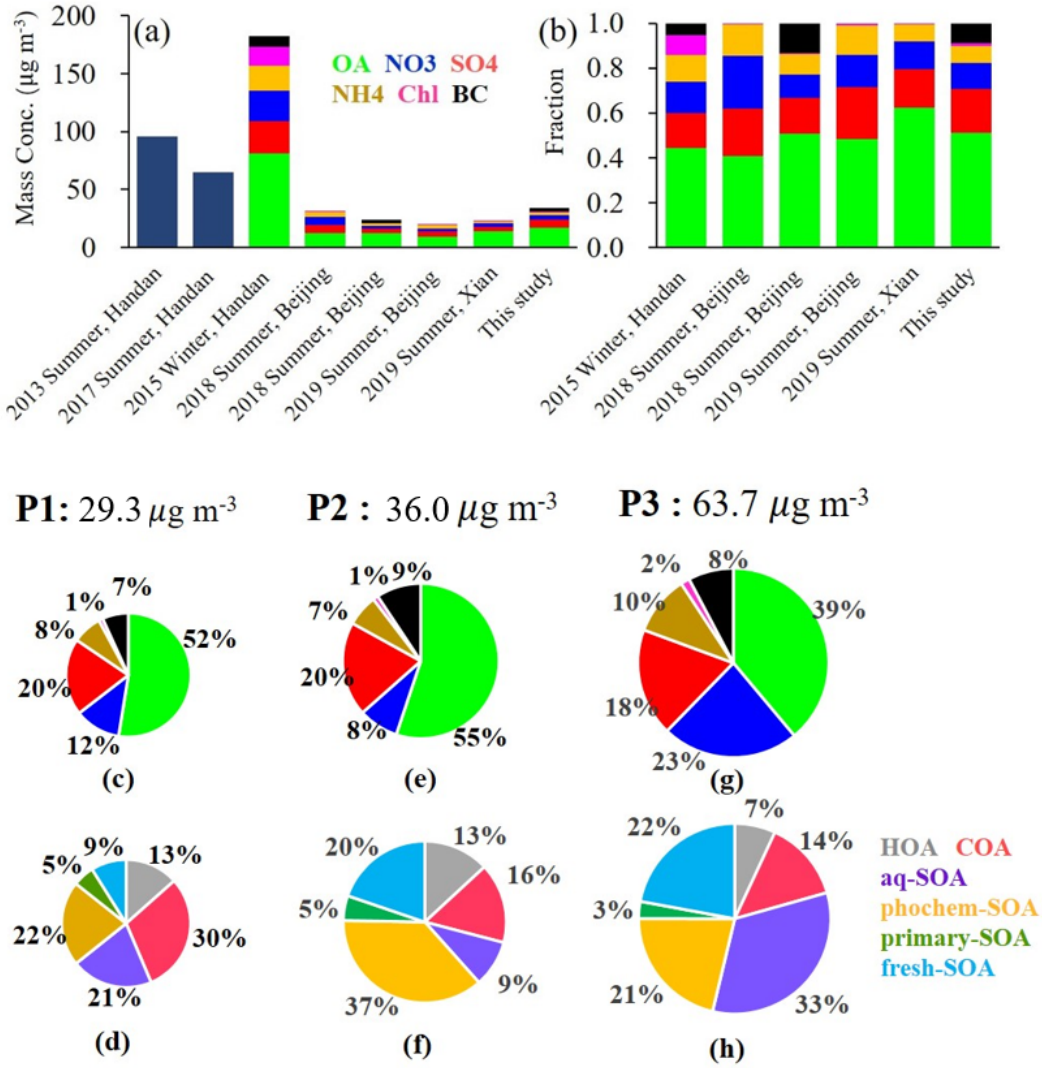


**Fig. S2** Concentrations (a) and fractions (b) of main chemical components in $PM_1$/$PM_{2.5}$ during summer and winter observations in NCP in recent years. The data and references are available in Table S2 of the Supplement. Fractions of main chemical components of $PM_{2.5}$ and OA in reference events (P1: c & d), high $O_x$ period (P2: e & f) and high RH period (P3: g & h).

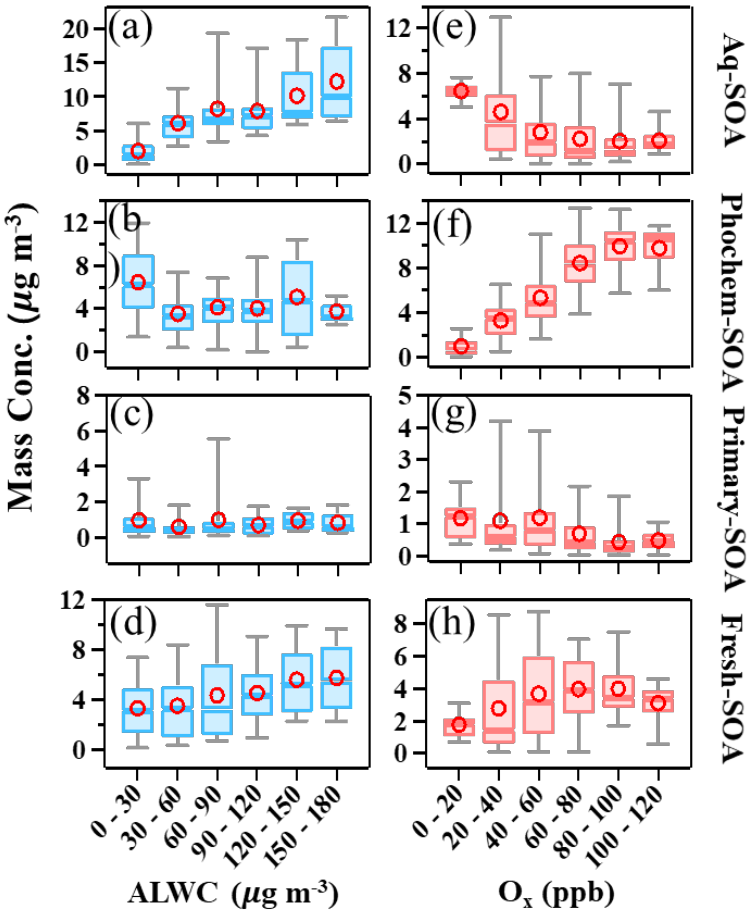


**Fig. S3** Variations of the mass concentrations of aq-SOA, phochem-SOA, primary-SOA and fresh-SOA as functions of ALWC (a~d) and $O_x$ (e~h). The data were binned according to the ALWC (30 $\mu$g m$^{-3}$ increment) or $O_x$ concentration (10 ppb increment), and mean (circle), median (horizontal line), 25th and 75th percentiles (lower and upper box), and 10th and 90th percentiles (lower and upper whiskers) are showed for each bin.

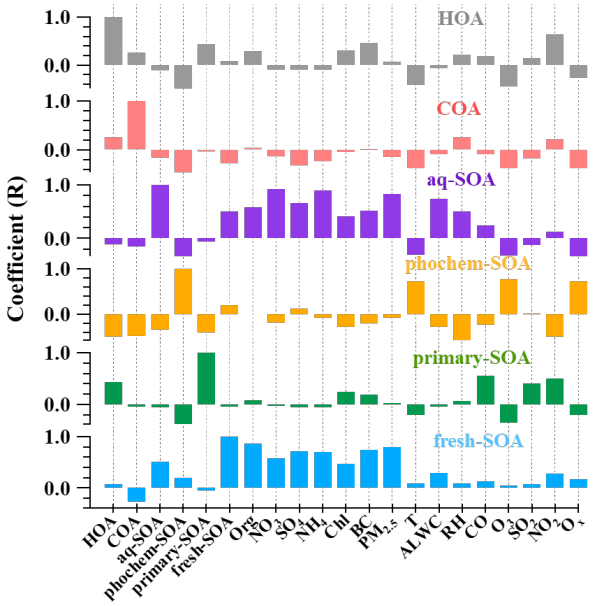


**Fig. S4** Correlation between the resolved OA factors and other chemical components in $PM_{2.5}$, gas-phase pollutants, and meteorological parameters.

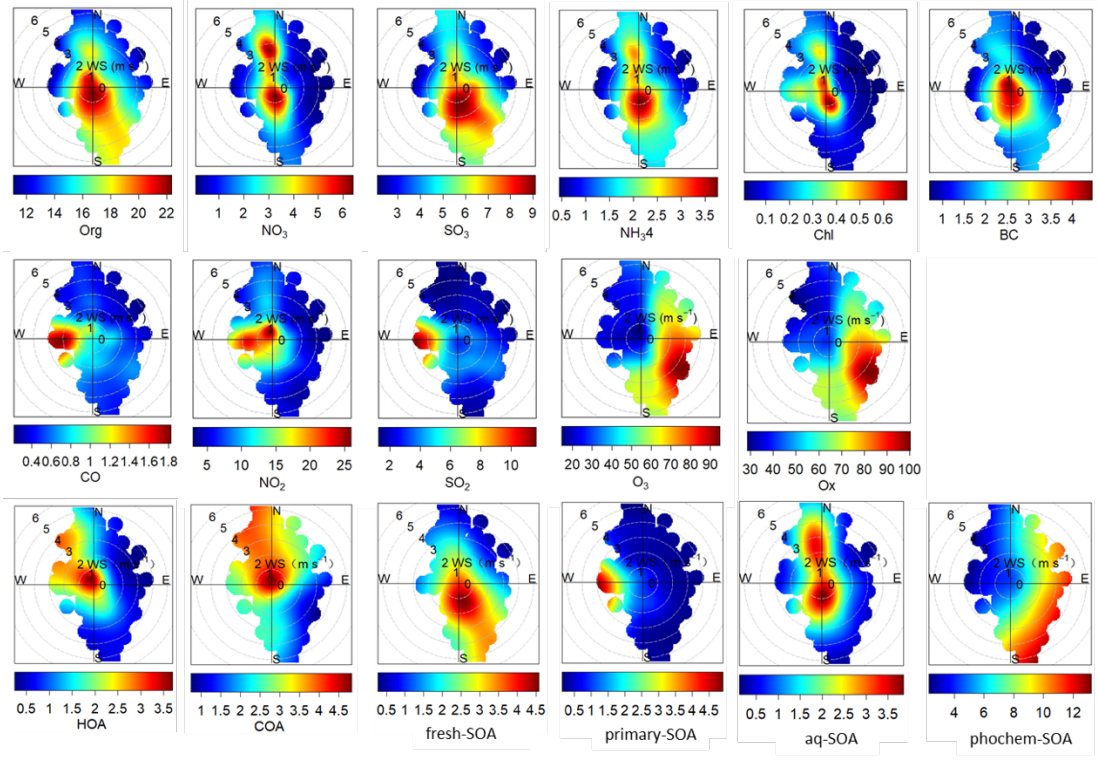


**Fig. S5** Polar plots that illustrate the variations of the hourly averaged concentrations of gases pollutants, $PM_{2.5}$ species and OA sources as a function of wind speed (m $s^{-1}$) and wind direction (°).

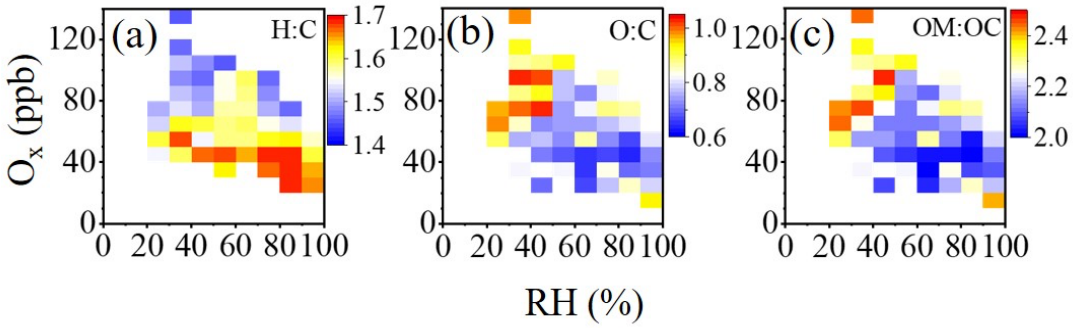


**Fig. S6** RH- and $O_x$-dependent distributions of (a) H:C, (b) O:C and (c) OM:OC ratios. Grids with the number of points less than five were excluded.

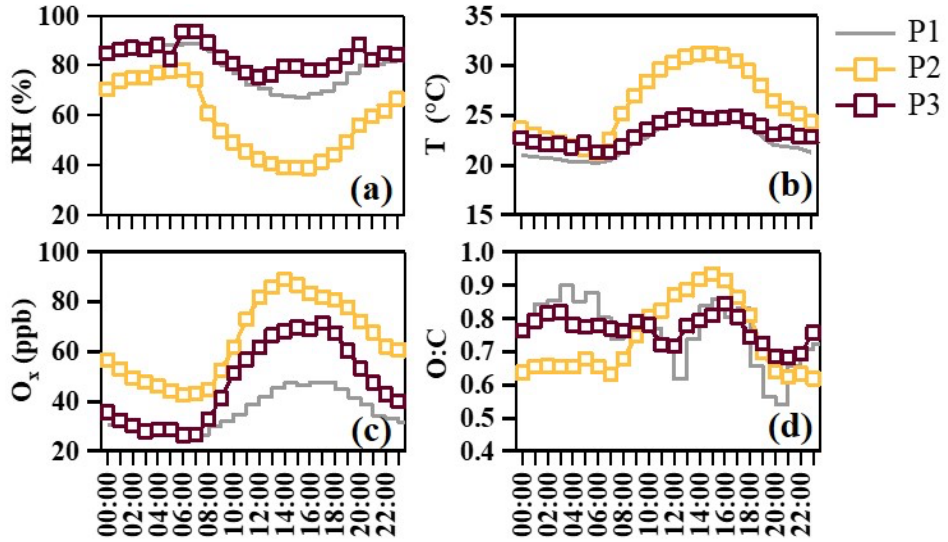


**Fig. S7** Diurnal patterns of (a) RH, (b) temperature, (c) $O_x$ and (d) O:C ratios in reference events (P1), high $O_x$ period (P2) and high RH period (P3).

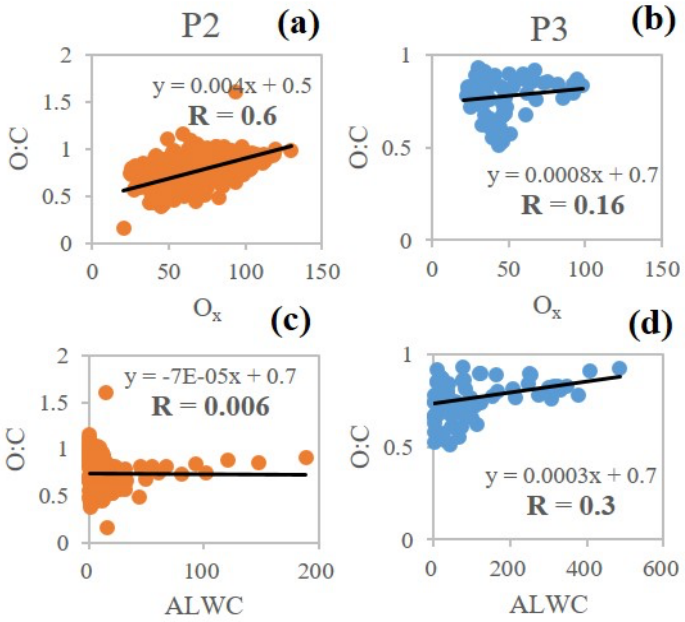


**Fig. S8** Relationship between O:C ratios and $O_x$/ALWC in high $O_x$ period (P2: a & c) and high RH period (P3: b & d) during this campaign.

**Supplementary information**

**1.1**

In the studied time period, POA (6.1 ± 3.61 $\mu$g m$^{-3}$) contributed 30.6% to the bulk OA, including the hydrocarbon-like OA (HOA, 12.2%) and cooking OA (COA, 19.1%) in summer of Handan. The results are consistent with the results in summer 2017 and 2018 from Beijing (Xu et al 2019b).

**HOA**

The spectrum of HOA is substantially contributed by alkyl fragments ($C_nH_{2n+1}^+$ and $C_nH_{2n-1}^+$, Fig. 1), major ions include $C_3H_7^+$, $C_4H^{9+}$, and $C_5H_{11}^+$ (Zhao et al., 2019; Xu et al., 2019a; Sun et al., 2016; Elser et al., 2016; Zhang et al., 2014; Ng et al., 2011), which is consistent with the previous studies (Canagaratna et al., 2004; Ng et al., 2010). HOA had a relative low O:C ratio of 0.14 and high H:C ratio of 1.77. On average, it accounted for 12.2% of total OA (Fig. S2a) in Handan, with the absolute concentration of 2.4 ± 2.1 $\mu$g m$^{-3}$, which was two times lower than that in Beijing (35%) at the same time period of 2018 (Chen et al., 2020a). The low HOA fraction was consistent with previous study, which revealed that transportation was a minor source of atmospheric particles in Handan compared to Beijing (Wang et al., 2014).

High correlations were also observed between the time series of HOA with BC ($R$=0.5) and $NO_2$ ($R$=0.6, Fig. S4), supporting the vehicle emission related origins of HOA reported in the previous studies (Lanz et al., 2007; Docherty et al., 2011). The polar plots (Fig. S5) demonstrated higher concentrations of HOA

under relatively low WS (< 2.0 m $s^{-1}$), which was very similar with BC, supporting the fact that HOA is a freshly locally-emitted vehicle OA. HOA exhibited slightly enhanced peaks in the morning (6:00-7:00 local time, LT) and prominent peaks during nighttime (19:00-22:00 LT) when the traffic jam happened (Fig. 6). However, these kinds of variations were less pronounced in P1 and P3 (Fig. 6), which might because the high WS and RH had influence to such local sources. Hence the stagnant meteorological conditions would result in accumulation of local sources during this measurement period. It should be noted that the fraction of HOA is lower during P3 (7%) compared with P1 and P2, this may be attributed to the large fraction of SOA (Fig. S2). The average HOA/BC ratio was 0.8, close to other cities in China e.g., Xianghe (0.91) (Sun et al., 2016), which was between those for diesel trucks (0.5) (Ban-Weiss et al., 2008) and light-duty vehicles (1.4).

**COA**

The COA mass spectrum was characterized by higher ratio than HOA between $f_{55}$ ($C_4H_7^+$+$C_3H_3O^+$) and $f_{57}$ ($C_4H_9^+$+$C_3H_5O^+$) (Mohr et al., 2012), and the spectral pattern was relatively constant among different years. The O:C and H:C ratios of COA were 0.18 and 1.57, respectively, suggesting their primary feature (Xu et al., 2016). On average, the mass contribution of COA to OA was 19.1% (Fig. S2a), which was close to that in the summer of 2018 (15%) in Beijing (Xu et al., 2019b).

The most pronounced feature of COA (Fig. 6) is its clearly enhanced diurnal peaks around morning (6:00–7:00), noon (12:00–13:00) and late evening (19:00–20:00), corresponding to the common meal hours which was consistent with previous studies of other regions of NCP (Sun et al., 2016; Sun et al., 2018;. During these meal hours, COA account for over 20% ~ 30% of total OA (Fig. S2d), signifying the importance of cooking sources in aerosol mass concentrations in urban areas of China.

Note that during the different periods, this mass fractions of COA to total OA present stable trend (14~16%) during P2 and P3, indicating that cooking styles remained consistent and local accumulation was not the major haze source during the measurement period (Fig. S2). While during the clean periods of P1 with wind, it increased to 30%, which was the largest contributor to OA. Moreover, the diurnal pattern of COA show very similar variations from three periods (Fig. 6) with the highest mass concentration during P1. This significant increase of COA is probably associated with the wind from southwestern where more residential areas with enhanced domestic cooking activities.

**1.2**

**Characteristics of SOA sources**

SOA accounted for 68.7% to total OA, four SOA factors were resolved depending on the oxidation state, which correspond to aged SOA and fresh SOA respectively (Jimenez et al., 2009). One factor is attributed to aqueous-phase chemistry (aq-SOA) and the other to photo-oxidation chemistry (phochem-SOA), while fresher factor is produced by fresh-source (fresh-SOA), and the other considered as oxidized

primary sources denoted as primary-SOA. Although all of the SOA factors were characterized by higher *m/z* 44 ($CO_2^+$) and *m/z* 28 ($CO^+$) signal, their mass spectrum and temporal trends were noticeably distinguishable, corresponding to different formation mechanism, which will be discussed in the following section.

**aq-SOA**

The aq-SOA was identified as it increased with ALWC but decreased with $O_x$ (Fig. S3), which might be produced in the aqueous-phase events and influenced by aqueous-phase chemistry. The aq-SOA exhibits the highest O:C ratios of all factors (0.7) and a higher $f_{CO2+}$ to the total signal of 21.7%, but a low H:C ratio of 1.24 (Fig. 1). On average, the mass concentration of aq-SOA consisted 15.2% of the total OA and 22.1% of the SOA (Fig. S2a, b). Good correlations were found between aq-SOA and nitrate ($R$= 0.9), as well as ammonium ($R$= 0.9, Fig. S4) (Zhang et al., 2007; Aiken et al., 2009 and Huang et al., 2010). The high correlation with nitrate may be attributed to their similar precursors and formation pathways. It is also clear that their polar plot patterns are similar (Fig. S5) with two originations of nitrate and aq-SOA were observed in our study. Results showed that the local origination associated with low wind speed (< 1.0 m $s^{-1}$) had a high concentration up to 4 $\mu$g $m^{-3}$, and the regional origination was associated with relatively high wind speed (> 2.5 m $s^{-1}$) derived from the northern regions (Fig. S5), suggesting that there were mixing regional and local sources for nitrate and aq-SOA. This supports the aq-SOA is relatively aged in ambient air and influenced by the combination of local formation and regional transport (Lanz et al., 2007; Hayes et al., 2013;Chen et al., 2021).

The aq-SOA contributed a major fraction of 33.3 % to the total OA during P3 (peak concentration: 25.2 $\mu$g $m^{-3}$; peak fraction: 65.3%), pointing the faster SOA production through aqueous-phase chemistry during this specific haze event compared to P1 (20.5%) and P2 (9.4%). In addition, the ALWC and aq-SOA were strongly correlated ($R$=0.7, Fig. S4), and both were shown dramatically enhancement during P3 event. This indicates that aq-SOA was either formed via aqueous phase reactions or absorbed/dissolved into aerosol liquid water. Previous studies also showed that high RH in summer facilitated the transformation of $HNO_3$ into aqueous-phase and increased nitrate concentrations substantially (Sun et al., 2013; Sun et al., 2015). Due to the high $NO_2$ concentration and high RH in this period, particulate nitrate was produced during this regional transport homogeneously and/or heterogeneously, resulting in water uptake and high LWC in the aerosol phase. The high ALWC in turn facilitated further heterogeneous formation of nitrate. This positive feedback provided favorable conditions for efficient aqueous chemistry and thus production of aq-SOA (Kuang et al., 2020). Note that the strong correlation between aq-SOA and ALWC was not driven solely by P3 event, rather, the two time series were remarkably well correlated throughout the entire campaign. This further supported the interpretation of aq-SOA as characteristic of aqueous SOA production throughout the campaign, rather than being characteristic of only a single event.

**phochem-SOA**

The phochem-SOA presented an opposite trend with significant increase as $O_x$ but decrease as ALWC (Fig. S3). $O_x$ has been shown to be a conserved tracer to represent photo-oxidation chemistry (Xu et al., 2017). The relationship between $O_x$ and photochemical SOA can offer insight into the formation mechanism of SOA associated with ozone production chemistry (Herndon et al., 2008). Therefore, when the mass concentration of phochem-SOA showed a substantial increase as a function of $O_x$, it could be likely due to the enhanced secondary transformation went from less oxidized to more aged with the progression of atmospheric photochemical aging, which were supported by the large $O_3$ fractions in $O_x$ in summertime (Zhang et al., 2019). Such conclusions were further supported by tightly tracked time series of phochem-SOA with $O_3$ ($R$ = 0.8) and $O_x$ ($R$ = 0.7) (Fig. S4). Considering $O_3$ has become the primary air pollutant in summertime in the NCP and had caused the enhancement of atmospheric oxidation capacity (Chen et al., 2020b), the photochemical processing driven by $O_3$ might play an important role in the formation of phochem-SOA.

The phochem-SOA had the highest average mass concentration of 6.1 ± 3.3 $\mu g\ m^{-3}$ among the OA factors, with the highest contribution to total OA (31%) and the SOA (45%) during observation time, suggesting the predominate role of this factor (Fig. S2). The phochem-SOA was oxidized with an O:C ratio of 0.67 and H:C ratio of 1.18, and it also had high $CO_2^+$ contribution of 17.9 %, which further suggested that the atmospheric oxidation capacity during summer was strong. Similar to aq-SOA, phochem-SOA also showed large variations during different periods. It accounted the most of 36.9% to OA during P2, compared to other two periods (21.5% in P1 and 21.3% in P3, respectively), indicating that the enhancement of phochem-SOA can leads to the development of SOA formation. The phochem-SOA also had the similar spatial pattern with $O_3$ and $O_x$ form the polar plots (Fig. S5), where high concentration associated with southeast wind originated from Shandong with relatively high wind speed of over 4 m $s^{-1}$, suggesting the typical feature of regional transport pollutants.

**primary-related-SOA**

In terms of two fresh SOA factors, they were defined as less oxidized OOA by relative lower O:C, stronger intensity of *m/z* 43 (mainly $C_2H_3O^+$) and *m/z* 44 (mainly $CO_2^+$).

The primary-SOA constituted the lowest contribution of 5% among all factors of the total OA and 7% of the SOA, however, it is still of particular interest in this study. It is characterized by both lower H:C (1.09) and O:C (0.54) ratios with $CO_2^+$ comprising 14.3%, which are higher than other POA factors, indicating a typical nature of less oxidized SOA. However, at *m/z* > 120, clear polycyclic aromatic hydrocarbons (PAHs) fragments are evident in mass spectrum of primary-SOA (Fig. 1), as indicated by the presence of similar patterns of PAH-like ions in their mass spectra 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 PAHs ions in POA spectrum, such as CCOA (coal

combustion) and BBOA (biomass burning) (Hu et al., 2016a;Zhao et al., 2019), but rarely in SOA. This observation implies that Primary-SOA may be link to the POA origin from domestic coal combustion (Xu et al., 2006). Through laboratory combustion studies using online aerosol mass spectrometry, they examined substantial ion signal at $m/z > 100$, which potentially link to the fragments of high molecular weight (HMW) species, was pronounced in both oxidized POA (OPOA) and POA, indicating that POA can be oxidized by multiphase reactions forming OPOA and the degradation of HMW species from the oxidation process (Budisulistiorini et al., 2021). In our study, the similar signatures of PAH-like ions was also found in aq-SOA at m/z > 150, but less pronounced in aq-SOA compared to Primary-SOA, consistent with previous study in Beijing (Wang et al., 2021). The observation of PAH-likes ions in both primary-SOA and aq-SOA further indicated they might both originated from coal combustion or transformation by oxidized POA, and the oxidation of PAHs being involved in the conversion of Primary-SOA to aq-SOA.

As it is shown in Fig. S4, primary-SOA exhibited relative better correlations with some gaseous pollutants, such as CO ($R$ = 0.6), $NO_2$ ($R$ = 0.5), and was also consistent with the temporal pattern of HOA ($R$ = 0.4), suggesting primary-SOA might be transformed from locally primary emissions. In addition, primary-SOA, had no significant increase trend with both ALWC and $O_x$ (Fig. S3), but its pollution pattern was similar as some primary precursors such as CO, $SO_2$ and $NO_2$, where higher concentrations appeared with weak west wind (Fig. S5). Therefore, the major pathway of this primary-SOA formation might be related to primary emission or the its transformation, which also supported by similar results obtained by Rivellini et al., (2020), who found the oxygenated part of combustion particles which was co-emitted with HOA and/or produced by oxidation of HOA rapidly could be oxygenated-HOA (O-HOA) or oxygenated-CCOA. Moreover, some SOA factors were defined as “urban-lifestyle SOAs” because it could derived from some POA exhaust such as vehicle and cooking through laboratory experiments (Zhang et al., 2021).

**fresh-SOA**

The fresh-SOA showed increase substantially as ALWC increasing, similar to aq-SOA. Whereas it also showed slight increase trend following $O_x$ when $O_x$ < 100 ppb (Fig. S3). Therefore, both aqueous-phase chemistry and photochemical processing were thought to have positive impacts synchronously on formation of Fresh-SOA. In this study, $CO_2^+$ comprised at least in Fresh-SOA of 8.3%, corresponding with the lowest atomic O:C ratio of 0.41 and a highest atomic H:C ratio of 1.41 among the four SOA factors. These characteristics consistent with the global average of LO-OOA of 0.35 ± 0.14, Ng et al., 2010), demonstrating the it is more fresh SOA. Besides, Fig. S2 showed that fresh-SOA consisted 18% of the total OA and 26% of the SOA. Note that the concentration of fresh-SOA increased in every event following with OA increased no matter the aqueous-phase event and photochemical event under the stagnant conditions. Meanwhile, it was well correlated with total OA ($R$ = 0.9), $PM_{2.5}$ ($R$ = 0.8) and BC ($R$ = 0.7, Fig. S4), as well as sulfate ($R$ = 0.7). The sustained contribution from fresh-SOA and

covariations between fresh-SOA with these species suggest that it was probably a mixed source which not just dominantly driven by only one formation mechanism. Nevertheless, different pathways among P1, P2 and P3 lead to the progressive fractions of fresh-SOA to total OA. Compared with P1, photochemical processing (P2) and aqueous-phase reactions (P3) strengthen to produce fresh-SOA individually, but the influence driven by aqueous-phase reactions is much greater than photochemical processing.

### 1.3 Evolution of OA

The mass spectra of these four factors for $PM_{2.5}$ are dominated by *m/z* 44 (mainly $CO2^{+}$) (Fig. 1). However, their concentrations show very different temporal variations. The concentration of aq-SOA correlates with NO3 ($R$= 0.9) and ALWC ($R$= 0.7), showing a steady increase as a function of ALWC (Fig. S4 and Fig. S3) which might indicate aqueous-phase chemistry. The aq-SOA exhibits the highest O:C ratio of all factors (0.7) and more aged oxidation state, while the O:C ratio of phochem-SOA remains high (0.67) but slightly lower compared to aq-SOA. The phochem-SOA presents an opposite trend with significant increase as function of $O_x$ but decrease as function of ALWC (Fig. S3), suggesting the photochemical formation and further supported by tightly tracked time series of phochem-SOA with $O_3$ ($R$ = 0.8) and $O_x$ ($R$ = 0.7) (Fig. S4). The mass spectrum of the fresh-SOA shows a high peak at m/z 43 (mainly $C_2H_3O^{+}$) (Fig. 1), corresponding to the lowest atomic O:C ratio of 0.41 and a highest atomic H:C ratio of 1.41 among SOA factors, which indicate its feature of fresher SOA. Note that the concentration of fresh-SOA increased in every period with OA increase, and was well correlated with total OA ($R$ = 0.9), $PM_{2.5}$ ($R$ = 0.8) and BC ($R$ = 0.7), as well as SO4 ($R$ = 0.7) (Fig. S4), indicating that they were freshly emitted and less oxidized. The primary-SOA in this study was of particular interest. It has relatively low O:C (0.54) and H:C (1.09) ratios, indicating a typical nature of less oxidized SOA. However, as shown in Fig. S4, primary-SOA exhibits relative better correlations with some gaseous pollutants, such as CO ($R$ = 0.6), $NO_2$ ($R$ = 0.5), and was also consistent with the temporal pattern of HOA ($R$ = 0.4), suggesting primary-SOA might be transformed from locally primary emissions.

### 1.4 VK Diagram

During this campaign, the H:C and O:C ratios in this study showed little variation, with average values of 0.75 ± 0.09 and 1.58 ± 0.28, respectively (Fig. 8a). The H:C ratio in Handan was slightly higher than that in Hong Kong (1.48) and Lanzhou (1.49) but lower than those at urban sites in Shenzhen (1.83), MongKok (1.83), Shanghai (1.92) and Jiaxing (1.94) (He et al., 2011; Huang et al., 2012, 2013; Li et al., 2015; Lee et al., 2015; Xu et al., 2016). Also, a general consistency was observed for the O:C ratio which was higher than mostly other sites, except the site in Oregon (US) influenced by wildfire. Overall, this relatively low H:C ratio, high O:C ratios suggested that OA in summer of Handan had higher degree of oxygenation than those at urban sites due to the progress of atmospheric photochemical aging, and also indicated the secondary portion having a substantial contribution to the bulk OA. Figure S5 shows a

synergistically impact of RH and $O_x$ to elemental ratios. For example, H:C increased with the decrease of $O_x$ concentration and with the increase of RH, which indicated that photochemical process had a positive effect but aqueous-phase process had an opposite effect on the H:C of atmospheric O. As for O:C, higher O:C ratio was mainly observed with high concentration of $O_x$, highlighting the importance of photochemical process in aerosol oxidation during summer. Meanwhile, slightly higher O:C also occurred at high RH levels even though the low concentration of $O_x$. Previous studies have demonstrated that aqueous-phase reactions of low-volatility high-molecular weight species detected in the atmosphere, such as glyoxal (Waxman et al., 2013), methyglyoxal (Lim et al., 2013), glycolaldehyde (Schöne and Herrmann, 2014), pyruvic acid (Altieri et al., 2006), and methacrolein (Liu et al., 2012), were the important formation pathway of OA (Kroll and Seinfeld, 2008; Hallquist et al., 2009; Sun et al., 2010; Chen et al., 2018). The products, such as highly oxygenated organic molecules (HOMs), from these aqueous-phase reactions would be conducive to elevating O:C (Molteni et al., 2018; Bianchi et al., 2019). On the other hand, the Fig. S7 showed that, the O:C ratio generally increased and the H:C ratio decreased during the day of 8:00–16:00 local time (LT), suggesting that SOA formation like photochemical process or mixing with more aged aerosols from regional sources was dominant during the day and outweighed the emissions POA (Sun et al., 2013).

To further investigate the pathways of OA factors, ions in the HR mass spectra were used to calculate the elemental ratios using the improved-ambient method (Canagaratna et al., 2015). The ratios were represented by the VK diagram in Fig. 8a (Heald et al., 2010) to show the OA evolution in the summertime of Handan. Based on our data, we found that HOA and COA factors (POA) are both located at the left-top corner with high H:C, low O:C and OSc below −1. Then, these POAs evolve toward the right bottom during the formation of SOA (Zhao et al., 2019). Functional groups are further added in Fig. 8a: only oxygen atoms to a carbon backbone results in a slope equal 0, while the replacement of a hydrogen atom with a carboxylic acid group (−COOH) results in a slope of −1 without fragmentation (Heald et al., 2010; Ng et al., 2011). As organic compounds are oxidized, a relatively flat slope of −0.19 for H:C versus O:C in this study suggests the importance of the addition of alcohol and/or peroxide (slope = 0) in OA aging with additional processes adding carboxylic acid and/or carboxyl groups. For SOA factors, Fresh-SOA factors are located in upper left region with high H:C and low O:C values compared with the other SOA factors. Although the primary-SOA has the lower O:C than other SOAs, it still located closely to these two SOAs，which further indicates they might have similar formation, compositions or transformation between these factors, which is consistent with the results from above section.

Table S3 present the comparison of average O:C (0.77 ± 0.1) and H:C (1.58 ± 0.1) for bulk OA in this study (three periods in Handan) with studies from China and other campaigns (four seasons in urban/suburban sites) based on the updated IA calibrations in Canagaratna et al. (2015). Briefly, OA in this study are at the higher end of O:C ranges reported in urban areas of China, and are comparable to

the O:C ratios at the suburban sites, suggesting the OA was fairly oxidized in summer in the urban Handan.

### 1.5 $f_{43}$ Versus $f_{44}$

Since the ion fragment with $m/z$ = 44 and 43 are usually originated from different functional groups and the ratio changes as a function of atmospheric aging, researchers usually use the triangle plot of $f_{44}$ versus $f_{43}$ to characterize OA evolutions in the atmosphere. As shown in Fig. 8b, POA and SOA factors fell into similar regions of $f_{44}$ versus $f_{43}$, suggesting that OA factors identified by PMF were fairly similar in the summertime of Handan. The bottom region of the triangle was dominated by POA factors (including HOA and COA) with low $f_{44}$ (about 0.05) and $f_{43}$ of 0.06 to 0.08, indicating that they were freshly emitted and less oxidized. Comparatively, SOA factors are located in different regions: (1) the fresh-SOA region with low $f_{44}$ (<0.10), indicating they were relatively less oxidized compared to other SOA factors. (2) the region with high $f_{44}$ (>0.17) than other OA factors, consistent with the fact that sq-SOA and phochem-SOA were surrogates of highly oxidized or regionally transported SOAs (Zhao et al., 2019); and (3) primary-SOA region, showing freshly oxidized properties ($f_{44}$ around 0.15). From the color plot of $f_{29}$ (mainly $f_{CHO+}$), $f_{CHO+}$ was observed highly correlated with formation of aged SOA factors.

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