Measurement report: Effects of photochemical aging on the formation and evolution of summertime secondary aerosol in Beijing

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Abstract. Atmospheric submicrometer aerosols have a great effect on air quality and human health, while their formation and evolution processes are still not fully understood. Herein, the crucial role of atmospheric oxidation capacity, as characterized by OH exposure dose in the formation and evolution of secondary submicrometer aerosols, was systematically investigated based on a highly time-resolved chemical characterization of PM1 in a southern suburb of Beijing in summertime from 25 July to 21 August 2019. The averaged concentration of PM1 was 19.3 ± 11.3 µg m−3, and nearly half (48.3 %) of the mass was organic aerosols (OAs) during the observation period. The equivalent photochemical age (t_a) estimated from the ratios of toluene to benzene was applied to characterize the OH exposure dose of the air mass, in which an observation period with the similar sources and minimal influence of fresh emission was adopted. The relationships of non-refractory PM1 species, OA factors (i.e., one hydrocarbon-like and three oxygenated organic aerosol factors) and elemental compositions (e.g., H/C, O/C, N/C, S/C, OM/OC, and OSc) to t_a were analyzed in detail. It was found that higher PM1 concentration accompanied longer t_a, with an average increase rate of 0.8 µg m−3 h−1. Meanwhile, the formation of sulfate and more oxidized oxygenated OA were most sensitive to the increase in t_a, and their contributions to PM1 were enhanced from 22 % to 28 % and from 29 % to 48 %, respectively, as t_a increased. In addition, OSc and the ratios of O/C and OM/OC increased with the increase in t_a. These results indicated that photochemical aging is a key factor leading to the evolution of OA and the increase in PM1 in summertime.

1 Introduction

Fine particulate matter (PM2.5) is one of the major atmospheric environmental problems, owing to its effects on air quality, human health, and climate (IPCC, 2013; Davidson et al., 2005; Molina and Molina, 2004). In recent years, the PM2.5 concentration in China exhibited a significant decrease with the implementation of the measures and strict policies in the Air Pollution Prevention and Control Action Plan (Zhang et al., 2019). However, the nationwide annual average concentration of PM2.5 is still greater than the standard of the World Health Organization (WHO) and PM2.5 is the primary pollutant in many regions, especially in the North China Plain (NCP). Beijing, one of the most polluted megacities in the NCP, is also facing severe PM2.5 pollution. The annual mean concentration in Beijing was 51 µg m−3 in 2018 (http://sthjj.beijing.gov.cn/, last access: 27 May 2020), which significantly exceeds the Chinese National Ambient
Air Quality Standard (annual average of 35 µg m$^{-3}$) and the WHO Standard (annual average of 10 µg m$^{-3}$). Continuing to reduce the PM$_{2.5}$ concentration is an important issue in improving the air quality in Beijing.

It has been well recognized that secondary aerosols (SAs), including secondary inorganic aerosol (SIA) and secondary organic aerosol (SOA), are the crucial constituents (30%–77%) of PM$_{2.5}$ (Xie et al., 2020; An et al., 2019; Sun et al., 2016a; Guo et al., 2014; Huang et al., 2014). However, the formation and evolution mechanism of SA is still not well understood, mainly due to multiple precursors, complex formation processes, and meteorological conditions (Chen et al., 2020, 2019a; Duan et al., 2020, 2019; Hua et al., 2018; Li et al., 2018a; Tie et al., 2017; Sun et al., 2015). Therefore, from the perspective of precise PM$_{2.5}$ control, in-depth understanding of the processes related to SA formation and evolution is crucial.

The Aerodyne high-resolution time-of-flight aerosol mass spectrometer (HR-ToF-AMS) has the advantage of real-time measurement of non-refractory submicrometer aerosol (NR-PM$_1$) with high time resolution and sensitivity compared to filter measurements (DeCarlo et al., 2006). As a result, HR-ToF-AMS measurements have been widely employed for illustrating the formation and evolution of PM in China (Chen et al., 2020; Xu et al., 2019b, 2014; Wu et al., 2018; Ge et al., 2017; Ye et al., 2017; Qin et al., 2016; Sun et al., 2016a; Huang et al., 2015; Li et al., 2015, 2013). Many previous field observation studies have inspected the formation mechanism and process of SA (Huang et al., 2019; Shi et al., 2019; Sun et al., 2018b, b, 2016b, 2014; Y. C. Wang et al., 2017, 2016; Xu et al., 2017; Cheng et al., 2016). For example, studies showed that an aqueous-phase process could be an important pathway in the formation of sulfate (Elser et al., 2016) and nitrate (Duan et al., 2020). However, most recent studies suggested that sulfate formation was also associated with a photochemical process, which is closely related to the meteorological conditions, especially in summertime (Chen et al., 2020; Duan et al., 2019). In terms of SOA, its contribution to PM$_{2.5}$ was reported to be as important as SIA during haze events in China (Huang et al., 2014). However, the formation mechanism of SOA is much less understood compared to SIA because SOA consists of various organic species with different oxidation degrees. Meanwhile, based on the organics database measured by HR-ToF-AMS, positive matrix factorization (PMF) analysis, one receptor model (Paatero and Tapper, 1994), has been employed to distinguish and quantify multiple OA factors (Hu et al., 2016; Sun et al., 2016b). Studies have found that photochemical and aqueous-phase processes played different roles in the evolution of SOA, which depended on the level of atmospheric oxidation capacity (e.g., total oxidant O$_3$ (= O$_3$ + NO$_2$)), relative humidity (RH), seasons, and regions (Chen et al., 2020; Feng et al., 2019; Y. C. Wang et al., 2017; Xu et al., 2017). For example, an aqueous-phase process was reported to have a significant effect on the formation of less oxidized oxy-gonated OA (LO-OOA) and more oxidized oxygenated OA (MO-OOA) at low levels of atmospheric oxidation capacity in wintertime Baoji, Shaanxi (Y. C. Wang et al., 2017). However, Xu et al. (2017) demonstrated that the formation of MO-OOA was significantly dominated by the aqueous-phase process, while LO-OOA was closely correlated with the photochemical process in urban Beijing (Xu et al., 2017). These inconsistencies highlight the necessity of studying the role of atmospheric chemical processes in the formation and evolution of different types of SOA.

Previous studies have revealed some important factors (e.g., seasonal variation, meteorological factors, and pollution degree) that influence the formation and evolution of PM$_1$ in Beijing based on AMS observations (Hu et al., 2016; Sun et al., 2013a, b, 2012; Zhang et al., 2014, respectively). Nevertheless, it should be pointed out that as the PM$_{2.5}$ concentration decreases, the ozone (O$_3$) concentration increases year by year (Li et al., 2019b; Zhang et al., 2019). O$_3$ has become the primary air pollutant in summertime in the NCP and has caused the enhancement of atmospheric oxidation capacity. Therefore, there is an urgent need to investigate the impact of these changes on the atmospheric oxidation capacity and the formation and evolution of PM$_1$. Moreover, it should be noted that most previous AMS observations in Beijing were carried out in urban areas (Duan et al., 2020; Xu et al., 2019b, 2017; Q. Wang et al., 2018; Li et al., 2017; Hu et al., 2016; Zhang et al., 2014; Sun et al., 2013a, b, 2012, 2010; Liu et al., 2012; Huang et al., 2010), while few studies were deployed in suburban areas (Chen et al., 2020; Li et al., 2019a). Considering the different meteorological factors and emission sources, the contribution of different formation and evolution pathways to PM$_1$ in urban and suburban areas could be different.

In this study, a field observation, mainly using HR-ToF-AMS, was conducted from 25 July to 21 August 2019 in a typical suburban site in Daxing District, which is the south gate of Beijing. The observation site lies in the air pollution transport channel between Beijing and Hebei province. Based on the measurement results of a series of gas- and particle-phase monitoring instruments, the chemical composition of NR-PM$_1$, elemental ratios, and source categories of OA were analyzed. Moreover, the formation and evolution of secondary aerosols were elucidated. Specifically, the effects of atmospheric oxidation capacity, which was characterized using the equivalent photochemical age ($t_a$), on the formation of secondary aerosols were discussed.

### 2 Experimental methods

#### 2.1 Sampling site

The online field observation was carried out in the top floor of a building (the ninth floor, ~27 m above the ground) at the Qingyuan campus of Beijing Institute of Petrochem-
ical Technology in Daxing District (39.73° N, 116.33° E) from 25 July to 21 August 2019. The site is located between the 5th Ring Road and the 6th Ring Road in the south of Beijing and is a typical suburban site. Additionally, there is no additional source of pollution except for two adjacent streets (i.e., Xinghua Street and Qingyuan Street, with a distance ~600 m). The aerosols and gases were sampled using a 1/4 in. stainless steel tube and 1/4 in. PFA tube, respectively, and the sampling inlet extended out of the window about 2.0 m (Fig. S1 in the Supplement). For the aerosol sampling line, the total flow rate was adjusted to 6.0 L min\(^{-1}\) using an additional pump to reduce the residence time of aerosols (~0.7 s). Meanwhile, an impactor with a size cut of 2.5 μm was equipped in the front of this sampling inlet to remove coarse aerosols. A series of gas analyzers shared the gas sampling line, and the total flow rate was about 5.5 L min\(^{-1}\) with a corresponding residence time of gas of ~0.8 s. During the field observation period, the average temperature and RH were 28.3 ± 3.3 °C (22.1–37.7 °C) and 62.0% ± 17.5% (21.7%–93.6%), respectively. The wind speed was in a range of 0.40 to 5.37 m s\(^{-1}\) with an average value of 1.62 ± 0.93 m s\(^{-1}\).

2.2 Instrumentation

The mass concentration and chemical composition of NR-PM\(_1\) were simultaneously measured by a HR-ToF-AMS (Aerodyne Research Inc., USA). The detailed principles of HR-ToF-AMS can be found elsewhere (DeCarlo et al., 2006). Briefly, the aerosols are dried using a diffusion dryer containing silica gel before they enter the HR-ToF-AMS to minimize the impact of aerosol liquid water on collection efficiency (CE). Following this, the aerosols are sampled through a critical orifice and then concentrated into a narrow beam via an aerodynamic lens. The size of aerosol is determined using the flight time of particles to the thermal vaporization and ionization chamber. Then the aerosols are successively vaporized by a heated surface (~600 °C), ionized by electron ionization (EI, 70 eV), and detected by a mass spectrometer detector. During this field observation, the HR-ToF-AMS was operated under alternation of two modes, i.e., 2 min V mode and 2 min W mode. The mass concentration of NR-PM\(_1\) was derived from V mode considering its higher sensitivity, and the elemental ratios were obtained from W mode due to its higher resolution. Meanwhile, routine quality assurance and quality control procedures, mainly including the calibration of inlet flow, ionization efficiency (IE), and aerosol sizing, were carried out regularly every week according to the standard protocols, using pure dry mono-dispersed 300 nm NH\(_4\)NO\(_3\) aerosols (Chen et al., 2019b; Drewnick et al., 2005) to guarantee the credibility of the HR-ToF-AMS results. The size distribution and number concentration of aerosols with a mobility diameter from 13.6 to 736.5 nm were also measured by a custom-built scanning mobility particle sizer (SMPS, Model 3082 equipped with 3776 CPC, TSI, USA). PM\(_1\) mass concentrations also calculated based on the volume concentration measured by SMPS and the estimated PM\(_1\) density (method details can be found in the Supplement). Its time series traced well with that from HR-ToF-AMS (\(R^2 = 0.91\); slope = 0.95 ± 0.01; see Fig. S2 in the Supplement).

The gas-phase species including NO\(_3\), SO\(_2\), O\(_3\), and CO were measured in real time by a series of Thermo analyzers (Model 42i-TL, 43i, 49i, 48i, respectively). The volatile organic compound (VOC) (e.g., benzene and toluene) concentrations were measured online using a vacuum ultraviolet single-photon ionization time-of-flight mass spectrometer (SPI-MS-3000, Guangzhou Hexin Analytical Instrument Co., Ltd., China). These instruments were calibrated periodically with the corresponding standard gas to ensure the accuracy of the observation data. In addition, the meteorological parameters including temperature (\(T\)), RH, and wind speed and direction were recorded by an automatic weather station (Vaisala M451).

2.3 Data analysis

2.3.1 HR-ToF-AMS data analysis

The standard analysis software tool (SQUIRREL, version 1.571 and PIKA, version 1.16I) written in Igor Pro (version 6.37, WaveMetrics Inc., USA) was used to analyze the HR-ToF-AMS data. In order to obtain the quantitative mass concentrations of different species (i.e., OA, SO\(_4\), NO\(_3\), NH\(_4\), and Cl), and considering that the aerosols were almost neutral and had been dried before entering into the HR-ToF-AMS inlet, the collection efficiency factor (CE) was determined according to the following equation (Middlebrook et al., 2012):

\[
\text{CE} = \frac{\max(0.45, 0.0833 + 0.9167 \cdot \text{ANMF})}{\text{ANMF}}
\]

where ANMF is the mass fraction of NH\(_4\)NO\(_3\) in NR-PM\(_1\). The default relative ionization efficiency (RIE) values were used for OA (1.4), NO\(_3\) (1.1), and Cl (1.3) (Jimenez et al., 2003). As for NH\(_4\) and SO\(_4\), their RIE values were determined using the pure dry mono-dispersed NH\(_4\)NO\(_3\) and (NH\(_4\))\(_2\)SO\(_4\) aerosols to be 4.0 and 1.2, respectively.

Elemental analysis (EA) was also executed using the “Improved Ambient” method (Canagaratna et al., 2015) to obtain the hydrogen-to-carbon ratio (H/C), oxygen-to-carbon ratio (O/C), and organic-mass to organic-carbon ratio (OM/OC), as well as elemental ratios of N/C and S/C. The average carbon oxidation state (OSC) can be approximated by 2 · O/C − H/C and is a metric describing the oxidation degree of atmospheric OA (Kroll et al., 2011).

2.3.2 PMF analysis of OA

Source apportionment of OA was executed using the PMF model to analyze the HR-ToF-AMS mass spectral data to identify the main organic components and their sources.
The HR-ToF-AMS mass spectra (PET, version 2.06) (Ulbrich et al., 2009) written in Igor Pro Q object function weighted two times, and with SNR in a range of 0.2–2 were weak variables and down to the values of the signal-to-noise ratio (SNR), m/z certainty (the number of samples, species, and factors, respectively. A least-squares fitting method was used to minimize the object function Q, which is defined as the sum of the squared residuals (eij) weighted by their degree of measurement uncertainty (σij).

\[ Q = \sum_{i=1}^{n} \sum_{j=1}^{m} (e_{ij}/\sigma_{ij})^2 \] (3)

In our study, the PMF software tool (PMF Evaluation Tool, PET, version 2.06) (Ulbrich et al., 2009) written in Igor Pro (version 6.37, Waveometrics Inc., USA) was used to analyze the HR-ToF-AMS mass spectra (m/z 12–170). The detailed steps have been expressed in Zhang et al. (2011). According to the values of the signal-to-noise ratio (SNR), m/z values with SNR in a range of 0.2–2 were weak variables and down-weighted two times, and m/z values with SNR less than 0.2 were bad variables and directly removed. As for duplicate information, m/z 44 (CO2) and related m/z values (including 16 (O), 17 (HO), 18 (H2O), and 28 (CO)) were also down-weighted. Then PMF was run for a range of factors (from 1 to 5) and rotational parameters (FPEAK) (from −1 to 1 with a step of 0.2). After considering multiple criteria, including mass spectral features, diurnal patterns, correlation with external tracers, and temporal variations (Zhang et al., 2011), the best number of factors was determined to be 4 (detailed diagnostics are shown in Fig. S3 in the Supplement), including one hydrocarbon-like OA (HOA) factor and three oxygenated organic aerosol factors (LO-OOA, IO-OOA and MO-OOA; IO-OOA is an abbreviation for intermediate oxidized oxygenated OA). The corresponding mass spectra, time series, and diurnal variation, which are similar to our previous results observed at the same site during summertime 2018 (Chen et al., 2020), are given in Fig. S4 in the Supplement.

2.3.3 Photochemical age

In the ambient air, the reaction of benzene and toluene with O3 and NO3 radicals is very slow, with reaction rates on the order of <10−20 and <10−16 cm3 molecule−1 s−1, respectively (Atkinson and Arey, 2003), which are significantly lower than the reaction rate with OH radicals (10−12 cm3 molecule−1 s−1). Thus, their degradation is dominated by reaction with OH radicals. Meanwhile, the reaction rate of toluene with OH radicals is about 5 times that of benzene. Therefore, their degradation rates in the ambient air are significantly different after being exhausted from an emission source, which would lead to an observable change in their concentration ratio. Consequently, the ratio of toluene to benzene is typically used to study the photochemical aging process of localized air masses (Yuan et al., 2012; Parrish et al., 2007; de Gouw et al., 2005; Gelencsér et al., 1997; McKeen et al., 1996).

In this study, the equivalent photochemical age (ta) was calculated to characterize the OH exposure dose of the air mass, as expressed in the following equation. This method had been widely used to provide useful information on the photochemical process in the atmosphere (Yuan et al., 2012; Parrish et al., 2007; de Gouw et al., 2005; McKeen et al., 1996).

\[ t_a = \frac{1}{[OH](k_{toluene} - k_{benzene})} \cdot \left[ \ln \left( \frac{[toluene]}{[benzene]} \right) \right] \] (4)

where [OH] is the average OH concentration in the ambient air and is assumed as 1.5 × 106 molecule cm−3 according to previous studies (Mao et al., 2009; Chu et al., 2016; Liu et al., 2018). k_{toluene} and k_{benzene} are the rate constants for the reactions of OH with toluene (5.63 × 10−12 cm3 molecule−1 s−1) and benzene (1.22 × 10−12 cm3 molecule−1 s−1), respectively (Atkinson and Arey, 2003). ([toluene]0/[benzene]0) is the emission concentration ratio of toluene and benzene before aging in the atmosphere and was determined to be 2.71 ± 0.39 (Fig. S6 in the Supplement) according to the methods described by de Gouw et al. (2017), where the ratio at night-time was used to avoid the impact of photochemistry and boundary layer dilution on the emission ratio. [toluene]0/[benzene]0 is the measured concentration ratio of toluene and benzene, as given in Fig. S6. Based on the back trajectories and air mass cluster analysis (Draxler and Hess, 1998) (Details can be found in the Supplement), an observation period (Cluster 2, Fig. S5 in the Supplement) with the similar emission sources was adopted. Furthermore, the data observed from 10:00 to 18:00 UTC+8 was used to minimize the influence of fresh emission during the morning and evening rush hours on t_a, as discussed by Qin et al. (2016). In this study, t_a was determined to be in the range of 4–90 h, which is comparable to previous studies (up to 72 h) conducted in China (Peng et al., 2016; Chu et al., 2021). Meanwhile, t_a had a higher level at noon, which is similar to the diurnal trend of OH radicals observed in summertime of Beijing (Tan et al., 2019).
the hourly mass concentrations of NR-PM$_1$ were in the range of 2.2–64.3 µg m$^{-3}$, with an average of 19.3 ± 11.3 µg m$^{-3}$, which is close to those observed in a suburb of Beijing in summer 2016 (14.2 ± 9.4 µg m$^{-3}$, Li et al., 2019a) and summer 2018 (24.1 ± 18.0 µg m$^{-3}$, Chen et al., 2020). However, this averaged PM$_1$ concentration was much lower than those observed in urban Beijing in summertime, such as 80 ± 40.6 µg m$^{-3}$ in 2006 (Sun et al., 2010), 63.1 µg m$^{-3}$ in 2008 (Huang et al., 2010), 50 ± 30 µg m$^{-3}$ in 2011 (Sun et al., 2012), and 37.5 ± 31.0 µg m$^{-3}$ in 2012 (Hu et al., 2017). Meanwhile, among all species in NR-PM$_1$, OA contributed the most (48.3 %), indicating the dominant role of OA in summertime PM$_1$ pollution (Chen et al., 2020; Hu et al., 2016; Sun et al., 2015; Zhang et al., 2014). Moreover, the largest daily contribution of OA (> 80 %) was observed during the clean period, with PM$_1$ concentrations less than 20 µg m$^{-3}$ (e.g., from 16 to 18 August 2019, Fig. 1b). On the other hand, SIA accounted for 51.7 % of NR-PM$_1$, in which sulfate was the largest contributor (23.2 %), followed by nitrate (14.3 %), ammonium (13.4 %), and chloride (0.8 %). Similar relative contributions of these species were also observed in a suburb of Beijing in summer 2016, where OA contributed a mass fraction of 42 %–71 %, followed by sulfate (15 %–27 %), nitrate (6 %–22 %), ammonium (8 %–13 %), and chloride (0.3 %–0.6 %) (Li et al., 2019a). The percentage of different chemical species in PM$_1$ reported in previous observations in summertime of Beijing in urban and suburban was compared in Fig. S7 in the Supplement. Typically, the fraction of OA (48.3 %) in suburban Beijing is higher than those in urban Beijing (33 %–38 %), while the contribution of SIA (51.7 %) in suburban Beijing is smaller than those in urban Beijing (58 %–64 %) (Hu et al., 2017; Huang et al., 2010; Sun et al., 2010, 2012). The reason may be the difference in the emissions of gaseous precursors (e.g., SO$_2$ and NO$_x$) and their conversion ratio to SIA (Hu et al., 2017; Li et al., 2020). Meanwhile, the inorganic sulfate, nitrate, and chloride could be well neutralized by ammonium during this field observation since there is an extremely good linear relationship between NO$_x$ + 2·SO$_4$ + Cl and NH$_3$ ($R^2 = 0.998$, slope = 0.992 ± 0.002, Fig. S8 in the Supplement). This implied the significant contribution of gaseous NH$_3$ to the formation of SIA and PM$_{2.5}$. Therefore, NH$_3$ emission control in China should be strengthened in the future to mitigate PM pollution (Liu et al., 2019b).

Figure 1 also presents the time series of total oxidant ($O_3 = O_3 + NO_2$) and photochemical age ($t_a$) in this study. $t_a$ and $O_3$ can be used to characterize the photochemical aging process undergone and the total oxidant present in the ambient atmosphere, respectively. As shown in Fig. 1c, $t_a$ showed a similar evolutionary trend to that of $O_3$, with a high correlation coefficient ($R^2 = 0.75$) during this summertime observation, implying there may exist a correlation between $O_3$ and $t_a$. It is well known that the photochemical aging process of VOCs can form organic peroxy radical (RO$_2$) and then accelerate the cycle of NO$_x$ and the formation of $O_3$ in the atmosphere. Therefore, a longer aging time ($t_a$) implies that more VOCs are consumed and more RO$_2$ is formed. Consequently, the transform cycles of NO$_x$ and the accumulation of $O_3$ would be accelerated under these conditions (T. Wang et al., 2017).

### 3.2 Role of photochemical aging in aerosol formation and composition

In order to evaluate the effect of the photochemical aging process, the relationships between $O_3$, PM$_1$, OA concentration, and binned $t_a$ were analyzed and shown in Fig. 2. These species concentrations all increase positively with the increasing of $t_a$. Meanwhile, with the increase in $t_a$, concentrations of PM$_1$ and $O_3$ increased simultaneously (Fig. 2 and S9 in the Supplement), suggesting that the photochemical aging process may have an important contribution to the formation of PM$_1$ and $O_3$ during summertime in Beijing. The possible reason is that high temperature in summer can volatilize more VOCs from biogenic sources (Fu et al., 2010) and anthropogenic sources (Pusede et al., 2014) (such as paint, as in McDonald et al., 2018, and asphalt, as in Khare et al., 2020), which could promote the formation of $O_3$ and PM$_1$ (Li et al., 2019c; Schnell and Prather, 2017). This was also verified by the positive correlation between $t_a$ and $T$ (Fig. S6). Further analysis showed that the concentration of $O_3$ significantly decreased with increasing NO$_x$ in this observation period (Fig. S9b), implying the VOC-sensitive regime of $O_3$ formation. Thus, increased VOCs will produce more RO$_2$ and $O_3$ locally (Li et al., 2018b), as well as more OA, since SOA (predominant species in OA) mainly originates from the photo-
NR-PM to be deeply explored to understand the growth of PM. OA were closely related to the photochemical aging process to the increased evaporation of IO-OOA (Hayes et al., 2013; observed in other field measurements and was mainly due to high concentrations of light alkenes during this period. These species will cause high O\textsubscript{3} during this period. These results also suggested that the photochemical aging process plays an important role in sulfate formation in the present summertime observation, as seen in Fig. S10 in the Supplement). The average increase rates in absolute mass concentration (Fig. S10 in the Supplement) showed the same trend as the normalized ratios in Fig. 4. The average increase rate of sulfate was the largest (0.4 µg m\textsuperscript{-3} h\textsuperscript{-1}) among NR-PM\textsubscript{1} species, while that of NR-PM\textsubscript{1} was 0.8 µg m\textsuperscript{-3} h\textsuperscript{-1}.

These results also suggested that the photochemical aging process plays an important role in sulfate formation in summer (Li et al., 2020). Previous studies have revealed that an aqueous-phase process plays an important role in sulfate formation (Sun et al., 2013, 2013a). However, it appears that photochemical oxidation was the primary pathway of sulfate formation in the present summertime observation, as seen in the t\textsubscript{a} and RH-dependent distributions of sulfate (Fig. S11 in the Supplement). Both the sulfate mass concentration and its proportion in PM\textsubscript{1} were highly dependent on t\textsubscript{a} rather than RH. As for nitrate, the corresponding ratio first increased and then slightly decreased as t\textsubscript{a} increased, which was similar to the evolution trend of absolute mass concentration (Fig. S10). It is worth noting that the concentration of NO\textsubscript{x} decreased with increasing t\textsubscript{a} (Fig. S12 in the Supplement), suggesting the photochemical oxidation of NO\textsubscript{x} to HNO\textsubscript{3} or nitrate. This was in agreement with the observation of high concentrations of NO\textsubscript{x} (NO\textsubscript{x} = NO\textsubscript{3}− + NO\textsubscript{2}−) at elevated t\textsubscript{a} levels (Fig. S12). Meanwhile, high temperature accompanied high levels of t\textsubscript{a} (Fig. S12), which could cause the evaporation of nitrate or adsorbed HNO\textsubscript{3} into the gas phase (Xu et al., 2019a). As demonstrated by the t\textsubscript{a} and RH-dependent distributions of nitrate (Fig. S11), the aqueous-phase process made a significant contribution to the formation of nitrate (Duan et al., 2020).

Regarding the OA factors, they exhibited different dependence on t\textsubscript{a} as presented in Fig. 4. Among these four OA fac-
Figure 3. Time series of OOA (= LO-OOA + IO-OOA + MO-OOA) and \( \text{O}_x \) (= \( \text{O}_3 + \text{NO}_2 \)). The inset is a scatterplot of OOA vs. \( \text{O}_x \) with linear fit and colored by the time of day. The regression slope is 0.130 (\( R^2 = 0.85 \)).

Figure 4. Variations of the ratios of mass concentrations of NR-PM\(_1\) species and OA factors to HOA as a function of \( t_a \). The data are binned according to the value of \( t_a \) (10 h increments). The solid lines are the results of exponential fitting with the function of \( y = A \cdot \exp(x/B) + C \).
DeCarlo et al. (2010). As shown in Fig. S14, the concentration ratio of organic aerosol and OOA (especially for MO-OOA) to ΔCO also increased significantly with $t_a$, which could be attributed to the SOA formation from the photochemical process and is also similar to the evolution trend of the ratios of OA components to HOA with $t_a$ (Fig. 4). These results further indicated the positive role of the photochemical aging process in aerosol formation.

Figure 5 shows the averaged contributions of NR-PM$_1$ species and OA factors at low and high $t_a$ levels. The average mass concentration of NR-PM$_1$ at $t_a > 40$ h was 25.3 µg m$^{-3}$, which was 1.4 times that at $t_a < 40$ h. All NR-PM$_1$ species were enhanced in mass concentration by a factor of more than 1.1 at elevated $t_a$, of which sulfate had the largest enhancement factor of 1.7. OA was the dominant species in $t_a$ from 48 % to 44 % with the increase in $t_a$. This indicated that photochemical aging is also similar to the evolution trend of OOA (especially for MO-OOA) to OOA (Peng et al., 2016; Chen et al., 2015; Ng et al., 2011; DeCarlo et al., 2010). As shown in Fig. S14, the concentration ratio of organic aerosol and OOA (especially for MO-OOA) to ΔCO also increased significantly with $t_a$, which could be attributed to the SOA formation from the photochemical process and is also similar to the evolution trend of the ratios of OA components to HOA with $t_a$ (Fig. 4). These results further indicated the positive role of the photochemical aging process in aerosol formation.

The OA factors also presented different change trends and different compositions at high $t_a$ levels compared with those at low $t_a$ levels. The OOA accounted for more than half of OA, and showed much higher contribution at high $t_a$ levels than at low $t_a$ levels (63 % vs. 80 %). Among them, MO-OOA showed the largest enhancement, by a factor of 1.7 from 3.2 to 5.3 µg m$^{-3}$ in absolute mass concentration and a factor of 1.6 from 29 % to 48 % in relative contribution, indicating the importance of MO-OOA in PM$_1$ pollution at elevated $t_a$ during the summertime. The contributions of LO-OOA and IO-OOA were almost equal (∼ 22 % and ∼ 10 %, respectively) between low and high $t_a$ levels, while the absolute mass concentrations were enhanced by a factor of > 1.1 at high $t_a$ levels. On the contrary, the absolute mass concentration of HOA decreased from 3.5 to 2.1 µg m$^{-3}$ during high $t_a$ periods, indicating a negative effect of $t_a$ on the accumulation of HOA. The effects of dilution and evaporation might also be another reason for the lower HOA contribution and concentration, which tended to be observed at higher temperature conditions and/or in the afternoon with the higher planetary boundary layer (PBL) (Fig. S9).

3.3 Role of photochemical aging in OA evolution

The role of $t_a$ in the evolution of OA during the summertime was further examined. Figure 6 shows the variations of H/C, O/C, N/C, S/C, OM$_1$/OC, and OSc as a function of $t_a$. All of these elemental ratios were determined from W mode due to its higher resolution. And all except H/C increased with the increase in $t_a$. The decrease in H/C was related to the decreased contribution of HOA (Fig. 5), since HOA had the highest H/C among these four OA factors (Fig. S4). In contrast to H/C, O/C and OM$_1$/OC increased from 0.52 to 0.77 and 1.88 to 2.20 with the increase in $t_a$, respectively. Moreover, a high correlation coefficient between OM$_1$/OC and O/C was observed ($R^2 = 0.997$, Fig. S15 in the Supplement). These results suggest that OA was highly oxidized due to the progress of atmospheric photochemical aging. Meanwhile, the analogous variation between OSc and O/C confirmed the high oxidation state of OA, since both are metrics of the oxidation degree of OA (Kroll et al., 2011). As for the variation of N/C and S/C, they presented a slight increase trend with the increase in $t_a$. This indicated that photochemical processes could contribute to the formation of N-containing and S-containing organics, which is consistent with the fact that both of them are the important products of gas-phase oxidation of VOCs and have also been detected in SOA (Farmer et al., 2010; Chen et al., 2019c, d).

The binned H/C and O/C as a function of $t_a$ are given in Fig. 7. The fitted slope of $-0.74$ is similar to those reported in both field observations and laboratory simulations on the photochemical aging of anthropogenic primary OA or biomass burning OA (Chen et al., 2015). This slope can be obtained by a combination of the simultaneous addition of both alcohol (slope = 0) and carbonyl (slope = −2) functional groups, or the addition of carboxylic acid with (slope = −0.5) and without (slope = −1) fragmentation (Peng et al., 2016; Chen et al., 2015; Ng et al., 2011;
Figure 6. Variations of H/C, O/C, N/C, S/C, OM/OC, and OSc as a function of $t_a$. The data are binned according to the value of $t_a$ (10 h increments).

Figure 7. Van Krevelen diagram during this field observation. The data are binned according to the value of $t_a$ (10 h increment) and color coded by $t_a$. The elemental composition of OA was fitted with a slope of $-0.74$ ($R^2 = 0.95$).
Heald et al., 2010). Additionally, as $t_a$ increased, the OA evolved from the top-left region to the bottom-right region of the Van Krevelen diagram, accompanied by a decrease in H/C and increase in O/C. This further indicated that the evolution process of OA was from less oxidized to more aged as the atmospheric photochemical aging progressed, leading to higher PM$_1$ concentrations.

4 Conclusions

In this study, a summertime field observation mainly based on the Aerodyne HR-ToF-AMS was carried out to characterize NR-PM$_1$ in a southern suburb of Beijing from 25 July to 21 August 2019. The role of photochemical age ($t_a$) in aerosol formation and composition was analyzed. During this period, the averaged NR-PM$_1$ concentration was 19.3 ± 11.3 µg m$^{-3}$. For NR-PM$_1$, OA was the dominant species (48 %–57 %), followed by sulfate (19 %–27 %) and nitrate (10 %–12 %) at different $t_a$ levels. Higher PM$_1$ concentrations were observed at longer $t_a$. Meanwhile, with the increase in $t_a$, the normalized ratios of NR-PM$_1$ species and OA factors to HOA were greatly enhanced by a factor of > 5, especially for OA, sulfate, and MO-OOA. The total NR-PM$_1$ presented the largest average increase rate of 0.8 µg m$^{-3}$ h$^{-1}$, followed by sulfate (0.4 µg m$^{-3}$ h$^{-1}$) and MO-OOA (0.3 µg m$^{-3}$ h$^{-1}$). As $t_a$ increased from 24.4 to 57.5 h, the relative contribution of MO-OOA presented the most obvious promotion from 29 % to 48 %, suggesting the significance of more oxidized OA, which mainly originates from the photo-oxidation of VOCs, in PM$_1$ pollution during the summertime with strong solar radiation. The evolution of OA was also greatly affected by $t_a$, decreased H/C and increased O/C could be found as $t_a$ increased, along with the larger OSc and OM/OC, indicating that OA went from less oxidized to more aged with the progression of atmospheric photochemical aging, further leading to the higher PM$_1$ concentration. Our results suggested that the atmospheric photochemical aging process is a crucial factor resulting in the PM$_1$ pollution in summertime, especially for the formation and evolution of SOA. Previous studies have indicated that NO$_x$ is a highly active species and has a great effect on the source of the main oxidants (e.g., OH, O$_3$, and NO$_2$) (Seinfeld and Pandis, 2016). VOCs, as the crucial precursors of SOA, are derived from a wealth of sources, as well as lack effective control methods relative to other precursors. Meanwhile, the relative change in emissions of VOCs has also been estimated to be increased by +11 %, while other precursors (mainly SO$_2$) decreased during the period of 2010–2017 (Zheng et al., 2018). The relative increase in VOCs would lead to the increased contribution of SOA in PM$_1$. Therefore, NO$_x$ and VOCs, mainly from vehicle-related emissions (Liu et al., 2019a; Qin et al., 2017), should be strictly controlled to lower the atmospheric oxidation capacity characterized by OH exposure dose to further ease the PM pollution in summertime. Meanwhile, more attention should be paid to the non-transportation sources, including heating (Cheng et al., 2018), cooking (H. Wang et al., 2018), asphalt-related emissions (Khare et al., 2020), and volatile chemical products (McDonald et al., 2018), which have been reported to be non-negligible contributors to ambient VOCs, and played a dominate role in the photochemistry of urban environments, especially for SOA formation.

Considering that there would be differences in the formation and evolution of PM$_1$ between different seasons, and few field observations have been conducted in suburban areas of Beijing, further work should be carried out to shed light on the seasonal variations of PM$_1$ and their formation and evolution mechanisms in different seasons in suburban areas. Additionally, the detailed role of photochemical age ($t_a$) in the formation of the secondary gaseous pollutant O$_3$, as well as their relationship in different seasons, should also be of concern because O$_3$ has become the primary air pollutant, especially in summertime.

Data availability. The experimental data are available upon request to the corresponding authors.

Supplement. The supplement related to this article is available online at: https://doi.org/10.5194/acp-21-1341-2021-supplement.

Author contributions. HH, YM, YL, and QM designed this field observation. TC, JL, and QM conducted the measurements and data analyses. TC, JL, QM, BC, PZ, CZ, and YL interpreted and discussed the data results. TC wrote the paper with input from all coauthors. All authors contributed to the final paper.

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

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References


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