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Changes in primary and secondary aerosols during a controlled Chinese New Year

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ABSTRACT

Large reductions in anthropogenic emissions during the Chinese New Year (CNY) holiday in Beijing have been well reported. However, the changes during the CNY of 2021 are different because most people stayed in Beijing to control the spread of coronavirus disease (COVID-19). Here a high-resolution aerosol mass spectrometer (HR-AMS) was deployed for characterization of the changes in size-resolved aerosol composition and sources during the CNY. We found that the reductions in traffic-related NOx and fossil fuel-related organic aerosol (OA), and cooking OA (1.3–12.7%) during the CNY of 2021 were much smaller than those in previous CNY holidays of 2013, 2015, and 2020. In contrast, the mass concentrations of secondary aerosol species except nitrate showed ubiquitous increases (17.6–30.4%) during the CNY of 2021 mainly due to a 4-day severe haze event. OA composition also changed substantially during the CNY of 2021. In particular, we observed a large increase by nearly a factor of 2 in oxidized primary OA likely from biomass burning, and a decrease of 50.1% in aqueous-phase secondary OA. A further analysis of the severe haze episode during the CNY illustrated a rapid transition of secondary formation from photochemical to aqueous-phase processing followed by a scavenging process, leading to significant changes in aerosol composition, size distributions, and oxidation degree of OA. A parameterization relationship between oxygen-to-carbon (O/C) and f_{44} (fraction of m/z 44 in OA) from a collocated capture vaporizer aerosol chemical speciation monitor (CV-ACSM) was developed, which has a significant implication for characterization of OA evolution and the impacts on hygroscopicity due to the rapidly increased deployments of CV-ACSM worldwide.

1. Introduction

The Chinese New Year (CNY) holiday has been widely used as a naturally controlled experiment to investigate the response of gaseous and particulate matter (PM) species to the changes in anthropogenic emissions (Jiang et al., 2015; Wang et al., 2017; Wang et al., 2021), and also the period of coronavirus disease (COVID-19) outbreak when the cities implemented lockdown measures (Dai et al., 2021; Javed et al., 2021; Sun et al., 2020). Previous studies have found ubiquitous reductions in aerosol and gaseous species from primary emissions during the CNY while secondary aerosol species showed less reductions and even increases due to enhanced secondary production. For example, Zhang et al. (2016) observed a clear increase in sulfate concentrations during the CNY due to a fog episode with strong sulfate formation. However, the sulfate concentrations were comparable before and during the CNY in winter of 2013 (Jiang et al., 2015). Sun et al. (2020) also found that the nitrate/sulfate ratios were comparable before and during the CNY although the decrease in NOx was more significant than SO2. These results demonstrated largely different responses of primary and secondary aerosol species to the changes in precursors under different conditions.
meteorological conditions during the CNY.

The anthropogenic emissions decreased substantially during the CNY due to the large decrease in the resident population. However, the CNY of 2021 is different because most people were encouraged to stay at home to control the spread of COVID-19. As a result, approximately seven million people who usually migrate from Beijing to their hometown stayed in Beijing in 2021, and the anthropogenic emissions from traffic and cooking activities were expected to be different from previous CNY. This provides a unique opportunity to investigate the characteristics of gaseous and aerosol species during a special CNY holiday. Particularly, previous studies were mainly based on the measurements of aerosol chemical speciation monitor (ACSM) with limited sensitivity and the absence of size information. Our knowledge of the size distributions, high resolution mass spectra, elemental compositions and sources of organic aerosol (OA) during the controlled CNY is far from complete.

In this work, a high-resolution time-of-flight aerosol mass spectrometer (HR-AMS) was used for the first time to study the changes in size-resolved aerosol composition, primary and secondary OA in Beijing during the controlled CNY. The comparisons of gaseous and aerosol species between clean and polluted days, and the formation and evolution of two severe haze episodes are elucidated. In addition, a PM$_{2.5}$ time-of-flight ACSM (Fröhlich et al., 2013) equipped with a capture vaporizer (CV) was also deployed simultaneously in this study. Because the additional thermal decomposition of CV results in the significantly high f$_{44}$ (fraction of m/z 44 in OA) compared to that of standard vaporizer (SV), the previously parameterized relationship between f$_{44}$ and oxygen-to-carbon (O/C) ratio needs to be re-evaluated. Hu et al. (2018) compared the elemental compositions of OA measured by HR-AMS equipped with a CV and SV, and a calibration parameter of O/C (0.73) was recommended. However, the estimation of O/C from f$_{44}$ of CV-ACSM has not been evaluated yet. Considering the wide deployments of CV-ACSM in measuring aerosol composition worldwide, we further develop a new relationship between CV f$_{44}$ and O/C which has a significant implication for better understanding the ageing and impacts of OA.

2. Materials and methods

2.1. Sampling site and instrumentation

All measurements were conducted at the Institute of Atmospheric Physics (IAP), a typical urban site in Beijing from January 17th to February 21st, 2021. A more detailed description of the sampling site was given in Xu et al. (2015). The entire study period was classified into before the CNY (BCNY, 17th January – 7th February) and CNY (8th – 21st February) according to the results of previous studies (Jiang et al., 2015).

Aerosol particles larger than 2.5 μm were first removed by a PM$_{2.5}$ cyclone fitted to the stainless steel sampling line (1 m long, ¼ inch outer diameter). After passing through a Nafion dryer at a flow rate of 1 L min$^{-1}$, the dried particles were sampled into the HR-AMS. Non-refractory submicron aerosol (NR-PM$_{1}$) species, including organics (Org), sulfate (SO$_{4}$), nitrate (NO$_{3}$), ammonium (NH$_{4}$) and chloride (Cl$^{-}$) were measured in the V-mode at a time resolution of 1 min. In addition, the NR-PM$_{2.5}$ species were measured by a CV-ACSM operated in parallel at a time resolution of 2 min, which was detailed in Zhou et al. (2022). SO$_{2}$, O$_{3}$, CO and NO$_{x}$ concentrations were measured by a suite of gas analyzers (models 43i, 49i, 48i and 42i, respectively, Thermo Scientific). The black carbon (BC) mass concentration at 880 nm obtained from a seven-wavelength Aethalometer (AE33, Magee Scientific Corp.) was used because the influences of brown carbon (BrC) and dust are negligible at this wavelength. Collocated measurements included relative humidity (RH), temperature (T), wind speed (WS) and wind direction (WD) at 103 m on the Beijing 325-m meteorological tower located 30 m away from our sampling site. The mixing layer height (MLH) was retrieved from the vertical attenuated backscatter coefficients measured by a single-lens ceilometer (CL51, Vaisala, Finland). In addition, the measurements of gaseous and PM species during previous CNY holidays in 2013, 2015, and 2020 (Sun et al., 2020) were used to explore the changes between controlled CNY and normal CNY in different years.

2.2. Calibration and calculations

The ionization efficiency (IE) was calibrated with 300 nm ammonium nitrate particles (Jayne et al., 2000; Jimenez et al., 2003), and the relative ionization efficiency (RIE) of NH$_{4}$ (4.42) was determined. The RIE of SO$_{4}$ (1.18) was determined from pure ammonium sulfate, and the default RIEs were applied for other species (i.e., Org, NO$_{3}$, and Cl$^{-}$). The composition-dependent collection efficiency was applied for the mass quantification (Middlebrook et al., 2012). The elemental ratios of OA were calculated by the "Improved-Ambient" method (Canagaratna et al., 2015). The mass concentrations of NR-PM$_{4}$ and NR-PM$_{2.5}$ were analyzed by using standard AMS data (SQUIRREL v1.64 and PIKA v 1.24) and ACSM data analysis software (ToFware v2.5.13, ACSM), respectively. The size distributions of secondary OA (SOA) were derived from that of m/z 44 because of its tight correlation with SOA, and those of primary OA (POA) were then obtained from the differences between the total OA and SOA (Zhang et al., 2005).

2.3. Positive matrix factorization (PMF)

Five OA factors were resolved from PMF (CU PMF Execute Tool (PET) v 3.05c) of high resolution mass spectra of OA (Paatero and Tapper, 1994; Ulbrich et al., 2009), including fossil fuel-related OA (FFOA), cooking OA (COA), oxidized POA (OPOA), oxidized OA (OOA), and aqueous-phase OA (aqOOA) (Figs. S1 and S2). A detailed description of the selection of PMF factors is given in supplementary (Text S1).

3. Results and discussion

3.1. Changes in aerosol species during CNY

Although the mean RH was comparable between BCNY and CNY (40.9% vs. 39.2%), and the temperature difference was small (4.8 °C vs. 1.0 °C), the frequencies of high RH (RH > 90%), 10.0% vs. 3.5%) and T (T > 0 °C, 22.6% vs. 10.3%) during the CNY were higher than those before CNY. The gaseous species showed large changes during the CNY. While NO$_{2}$ and NO decreased by 7.6% and 34.4%, respectively, SO$_{2}$ showed an increase of 23.4% during the CNY demonstrating the different changes in anthropogenic emissions. We also noticed a slight increase of MLH (568 m vs. 698 m) during the CNY which would affect the comparisons between BCNY and CNY.

The changes in aerosols species during the CNY were also different. For example, sulfate increased by 30.4% from 5.5 μg m$^{-3}$ before the CNY to 7.2 μg m$^{-3}$ during the CNY (Table S1). Such an increase was attributed to faster oxidation of SO$_{2}$ during the CNY due to a severe haze episode with high RH > 90% (Fig. S3). In comparison, the mean concentration of NO$_{2}$ was comparable before and during the CNY (14.4 μg m$^{-3}$ vs. 14.2 μg m$^{-3}$), and the diurnal cycles of NO$_{2}$ were also similar (Fig. S4). An explanation was that the reduction in NO$_{x}$ emissions (<35%) caused a higher potential for nitrate formation during the CNY as indicated by the higher nitrogen oxidation ratio (NOR, molar fraction of nitrate in total nitrogen, i.e., nitrate + NO$_{2}$). Although the nitrate-to-sulfate ratio decreased from 2.7 before the CNY to 2.0 during the CNY, NO$_{2}$ still exceeded OA and became the dominant component in PM$_{1}$ (≥NR-PM$_{1}$ + BC, 34%), supporting the significant role of nitrate in air pollution (Li et al., 2018; Xu et al., 2019; Zhou et al., 2020). Similarly, the three SOA factors changed substantially from BCNY to CNY (Fig. 1). For example, aqOOA decreased from 2.8 μg m$^{-3}$ before the CNY to 1.4 μg m$^{-3}$ during the CNY, and the fraction of aqOOA in OA decreased
correspondingly from 22.8% to 9.6%. Although aqOOA was highly correlated with SO$_4$ during both BCNY and CNY, the slopes of aqOOA vs. SO$_4$ were different (Fig. S5). Such differences likely indicate the different aqueous-phase processing between BCNY and CNY, yet it is challenging to separate them by AMS-PMF. For instance, the high RH event during the CNY lasted approximately two days with the temperature above 0$^\circ$C, while the aqueous-phase processing before the CNY occurred at a temperature close to 0$^\circ$C. A recent study by Xu et al. (2021a) found substantially different evaporative loss of more oxidized oxygenated OA (MO-OOA) across different RH levels likely due to the changes in molecular composition under different RH levels. Chen et al. (2020b) also separated SOA into different factors associated with different chemical processing. Comparatively, the OOA and OPOA concentrations increased by 34% and 176%, respectively during the CNY likely due to the enhanced photochemical processing which was supported by the higher frequencies of high O$_3$ level (>30 ppb, 9.8% vs. 29.0%). Note that the change percentages of secondary inorganic aerosol (SIA) varied from 1.3% to 30.4%, which were overall lower than that of SOA (33.0% and 32.3%), highlighting the dominant role of secondary formation during the CNY. These results suggest that mitigation of secondary aerosol formation over a regional scale is crucial for air pollution control in the future, particularly under a condition of enhanced atmospheric oxidizing capacity (Feng et al., 2021).

Although secondary aerosols changed substantially during the CNY, the concentrations of POA stayed relatively constant. For example, the mass concentrations of COA were similar between BCNY and CNY (2.4 μg m$^{-3}$ vs. 2.3 μg m$^{-3}$), consistent with the fact that few people left Beijing during the CNY. The FFOA concentrations were also comparable between BCNY and CNY (2.2 μg m$^{-3}$), however, BC showed an increase by 42%. As indicated in Fig. 1, BC presented similarly high concentrations as secondary species during haze episodes, while the concentration of FFOA was relatively low. These results indicated that a large fraction of BC in Beijing could be from regional transport rather local emissions (Sun et al., 2016b; Wang et al., 2016). This is further supported by the high correlation between BC and SIA before and during the CNY (Fig. S6). Note that the contributions of species related to primary emissions to PM$_1$ increased by 22.7% during the CNY, which was lower than that of SIA (33.0%) and SOA (32.3%), highlighting the dominant role of secondary formation during the CNY. These results suggest that mitigation of secondary aerosol formation over a regional scale is crucial for air pollution control in the future, particularly under a condition of enhanced atmospheric oxidizing capacity (Feng et al., 2021).

The changes in primary species in winter of 2021 showed large differences from previous CNY when primary species, e.g., BC and POA showed ubiquitous decreases. These results demonstrate that the changes in anthropogenic activities have direct impacts on primary aerosols. This is further supported by the much higher POA-to-SOA ratios across different RH levels in winter of 2021 than those in 2020 (Fig. S7). We further compared the holiday effects on the changes in aerosol species across different RH levels in 2020 and 2021. NO$_3$/SO$_4$ showed an obvious increase at low RH levels while a decrease at high RH levels from BCNY to CNY in winter of 2021, implying that the changes of NO$_3$/SO$_4$ were strongly RH dependent. However, the NO$_3$/SO$_4$ showed an increase at high RH during the CNY in 2020. These results suggested that the increased atmospheric oxidation had facilitated the nitrate formation in 2020 despite the large reductions in NO$_x$ (Huang et al., 2020). Overall, the changes in SIA and SOA concentrations during the CNY varied largely different among different years due to the changes in precursors and meteorological conditions. For example, the SOA-to-SIA ratio were comparable between BCNY and CNY (0.28 vs. 0.31) in 2021, while the increases were found during the CNY of 2013, 2015 and 2020,
and the decreases in 2018 and 2019. These results suggest that the chemical responses of SOA and SIA to precursor changes under the similar emission control measures can be significantly affected by meteorological conditions. As shown in Fig. 57, the increases in SOA/SIA during the CNY were observed in 2020 across different RH levels, which was different from that in 2021, suggesting that the changes in precursors had more impacts on the formation of SOA than SIA. Note that the SOA-to-SIA ratio during this study were lower than those before 2021 (Sun et al., 2020). One reason is that the SOA determined from CV-ACSM was higher than that from SV-AMS due to the strong thermal decomposition in the vaporizer. In fact, Zheng et al. (2020) also found that the SOA from the CV-ACSM on average accounted for 60% of OA, while that from SV-AMS only contributed 40% to OA.

3.2. Changes in aerosol species on clean and polluted days

The PM4 concentrations increased by 21.6% during the CNY of 2021 on clean days (PM$_{2.5}$ < 35 µg m$^{-3}$), and the increase was much higher than that on polluted days (6.0%) (PM$_{2.5} > 35$ µg m$^{-3}$). Comparatively, the PM$_{2.5}$ concentrations showed overall increases on clean days, whereas it showed decreases on polluted days during the CNY from 2012 to 2020 due to the reductions in primary emissions (Sun et al., 2020). The changes in PM4 species also varied largely among different PM levels in winter of 2021. For example, the increases in Chl and BC during the CNY on polluted days were much higher than clean days, which could be partly attributed to the contribution of regional transport from the south and southwest. Comparatively, nitrate showed a slight increase on clean days, yet a decrease on polluted days (28.3 vs. 24.0 µg m$^{-3}$). In contrast, the changes in SO$_4$ during the CNY of 2021 were comparable between clean and polluted days, while obvious increases in SO$_4$ were observed in previous years on polluted days (Sun et al., 2020). The changes in gaseous precursors were also different between clean and polluted days in winter of 2021. While NO$_2$ showed decreases on both clean and polluted days by 3.7% and 15.1%, respectively, SO$_2$ increased by 2.8% and 29.0%, respectively instead. Such changes in NO$_2$ and SO$_2$ were different from nitrate and sulfate, indicating the nonlinear relationships between PM4 species and precursors. As a result, the PM compositions changed more significantly during the CNY of 2021 on polluted days than clean days. For example, NO$_2$ exceeded OA before CNY (37.9% vs. 27.3%), while it was comparable to OA during the CNY (30.4% vs. 29.7%) on polluted days. Comparatively, the contribution of NO$_2$ to PM4 was similar before and during the CNY on clean days.

The increases in OA during the CNY of 2021 were insignificant on both clean and polluted days which was different from previous years showing ubiquitous decreases, particularly on polluted days (Sun et al., 2020). The different responses of SOA and POA across PM levels were also observed. For example, COA and FFOA showed similar mass concentrations before and during the CNY on both clean and polluted days in winter of 2021, which were much different from previous studies showing more reductions in primary emissions on polluted days than clean days. In addition, the average increase in OOA concentration was more significant on clean days than polluted days during the CNY 2021, which was different from OPOA that showed more increases on polluted days. Such differences were likely due to the fact that OPOA was related to primary emissions (e.g., BC and Chl) which showed significant increases on polluted days (Fig. 58). In addition, the reduction in nCnOAA during the CNY of 2021 on polluted days was more significant than clean days. Accordingly, the POA-to-SOA ratio decreased from 0.97 to 0.55 during the CNY on clean days, while the change was relatively small on polluted days (0.50 vs. 0.40). Overall, the fraction of SOA on clean days increased by 13.6% during the CNY, which was larger than that during polluted days (4.4%). In contrast, the SIA fractions showed decreases from 65.3% to 58.5% on polluted days, while slight increases on clean days.

3.3. Size distributions

The mean peak diameter of organics shifted slightly from 448 nm before CNY to 427 nm during the CNY, which was comparable to previous results in winter in Beijing (Xu et al., 2021b). POA peaked at 350 nm before and during the CNY and dominated the OA composition at small size ranges (Figs. 59–10) indicating the importance of primary emissions in formation of small particles (Hu et al., 2016; Xu et al., 2015). Comparatively, the SOA concentrations during the CNY were ubiquitously higher than those before the CNY across all sizes, yet the increases varied differently at different sizes. One explanation is the SOA at different sizes can be from different formation mechanisms. For instance, previous studies found that the SOA from photochemical production showed a dominant contribution in small size ranges, while that in large size was dominantly from regional processes (Xu et al., 2021b). The peak diameter of NO$_2$ was 448 nm before and during the CNY, which was slightly smaller than that observed in previous winters in Beijing (Hu et al., 2017; Xu et al., 2019). In contrast, the peak diameter of SO$_4$ shifted to large sizes from 566 nm to 592 nm likely due to the enhanced sulfate formation during Ep2. As shown in Fig. S11, the NO$_2$/SO$_4$ showed a decreasing trend as a function of size, indicating the increasing role of SO$_4$ in large particles. Nevertheless, the ubiquitously higher nitrate-to-sulfate ratios than unit demonstrated the more importance of nitrate in PM pollution than sulfate across all sizes.

The size distributions of aerosol species were largely different between clean and polluted days. As shown in Fig. 2, the OA peaked at 350 nm and 400 nm before and during the CNY, respectively, on clean days, while the peak diameter shifted to 516 nm and 470 nm, respectively on polluted days. Similarly, the peak diameter of SO$_4$ shifted from 448 nm on clean days to 620 nm on polluted days, and that of nitrate shifted from 230–400 nm to 516 nm correspondingly. These results are overall consistent with previous studies showing rapid growth of particle sizes due to the increased RH and enhanced secondary formation during the evolution of haze episodes.

3.4. Elemental ratios

The mean O/C was 0.54 before the CNY (Fig. S12), which was higher than that previously reported in winter in Beijing (0.37–0.45) (Sun et al., 2016a; Xu et al., 2019), likely suggesting the increase of oxidation capacity in recent years (Chen et al., 2020a; Lei et al., 2020). The O/C of OA increased by 10% from BCN to CNY indicating that the OA was slightly more aged during the CNY.

The OA at RH < 20% was mainly located on the left corner of triangle plot (Ng et al., 2010) with the relatively unchanged $f_{34}$ (0.05–0.07) and a wide range of $f_{44}$ (0.05–0.25), indicating large variations in OA oxidation degree. Comparatively, OA at high RH levels evolved towards the upper left corner with a decrease in $f_{34}$ and an increase in $f_{44}$ suggesting the ageing of OA as the increase of RH. However, we also found that the OA at RH > 90% was located in the middle of triangle region, which was consistent with previous studies in Beijing (Zhao et al., 2019). This result further demonstrated that aqueous-phase processing produces SOA with moderately high $f_{34}$ and $f_{44}$. The slopes of hydrogen-to-carbon ratio (H/C) vs. O/C also changed at different RH levels, suggesting the different OA evolutionary mechanisms (Heald et al., 2010). As shown in Fig. 5, the slope was −0.83 at low RH levels (RH < 40%), and OA was aged mainly via addition of carboxylic acids without fragmentation. In contrast, much flatter slopes of −0.40 and −0.27 were found at RH = 40%–90% and RH > 90%, respectively, indicating the rapid increases in O/C with small changes in H/C. Such flat slopes indicated the ageing of OA with addition of alcohol or peroxide functional group. In particular, OA formed through aqueous-phase processing showed both relatively high H/C and O/C ratios.
3.5. Haze episode analysis

The evolution of aerosol composition, size distribution and elemental composition before and during the CNY was further investigated by analyzing two severe haze episodes (Fig. 1). The first haze episode (Ep1) was observed during 19th–26th January and the PM$_{1}$ concentration reached as high as 142 μg m$^{-3}$. Aerosol species first showed rapid increases and then remained relatively stable except two sudden decreases in the middle due to the effect of mountain-valley winds. Aerosol composition was also relatively stable and dominated by nitrate (39%) and OA (27%). Such variations suggested the similar evolutionary mechanisms of secondary species during Ep1 and relatively stable primary emissions as indicated by the constant BC-to-CO ratio (2.9). In addition, the mean peak diameters of PM$_{1}$ species were similar varying between 490 nm and 570 nm, likely suggesting the internally mixed particles during Ep1.

The second haze episode (Ep2) can be classified into four stages according to the changes in aerosol compositions and mass concentrations. The low RH (<40%) and high concentrations of nitrate and OOA during the formation stage (S1) together indicated that photochemical processing was the major evolutionary mechanism. The PM$_{1}$ concentrations showed further increases during the secondary stage of Ep2 (S2) associated with a change of WD. OA and nitrate concentrations reached as high as 41.6 and 45.0 μg m$^{-3}$, respectively, accounting for 29.8% and 32.3% of PM$_{1}$. The shallow slope of H/C vs. O/C ($0.25$) suggested a more important pathway of addition of alcohol or peroxide functional group in OA formation. The third stage (S3) was characterized by high RH and large increases in sulfate and aqOOA, yet the nitrate concentration decreased slightly. These changes in chemical compositions highlight the impact of aqueous processes on aerosol compositions. The O/C showed further increases from 0.44 during S1 to 0.73 during S3, and the formation of SOA with hydroxyl group or oligomers through aqueous-phase processes could explain the elevated O/C. Also, the peak diameters of OA shifted from 350 nm during S1 to 566 nm during S3, suggesting the hygroscopic growth of aerosol particles as the increase of RH. Such increases in peak diameters were also
observed for nitrate and sulfate, which were 600 nm and 650 nm, respectively, during S3. The fourth stage (S4) showed an obvious difference from previous stages because it was affected by a snow-rain event. The PM1 concentration decreased to 45.1 μg m⁻³ due to the effect of wet scavenging (Sun et al., 2013). Although the total SOA fraction had almost no change from S3 to S4, an increase in OOA fraction and a decrease in aqOOA fraction were observed. One reason is that aqOOA is more water-soluble (Qiu et al., 2020) and could be scavenged more efficiently by the precipitation. Accordingly, the O/C of OA decreased to 0.71. Note that sulfate exceeded nitrate and OA, and dominated chemical compositions during S4. The peak diameters of nitrate and sulfate were similar (620 nm) during S4 likely indicating that they were internally mixed. This is further supported by the relative stable NO₃/SO₄ across different sizes (Fig. S7). The ratios of combustion tracers also showed differences in different stages. For example, the BC-to-CO ratio was 4.7 and 5.5 during S1 and S2, respectively, and then decreased to 2.8 and 1.1 during S3 and S4. Such results suggest the changes in primary emissions in different stages, which was also supported by the decreasing trend of NO₃/CO from 48.0 to 6.8 during Ep2.

3.6. Estimation of O/C using CV-ACSM $f_{44}$

The OA measured by CV-ACSM and RH dependence of the relationship between O/C and CV-ACSM $f_{44}$ are shown in Fig. 4. The significant correlation between $f_{44}$ and O/C was observed except for the conditions with high RH (RH > 80%) and low OA (OA < 10 μg m⁻³). The weak correlations under high RH levels were likely due to the variations of OA compositions. For example, the increases in organic compounds containing CHO⁻ measured by SV-AMS under high RH levels could increase O/C, while such changes in ions might not be reflected by the CV-ACSM $f_{44}$. In fact, the correlations of AMS O/C and AMS $f_{44}$ also varied as a function of RH (Fig. S13). In particular, the correlation during periods with RH > 90% was weaker and the slope was higher. Note that the correlation between O/C and $f_{44}$ measured by CV-ACSM was lower than that measured by SV-AMS (Atken et al., 2008; Canagaratna et al., 2015), which was likely caused by the fact that the increased fragmentation in the CV resulted in the significant signals of $f_{44}$ in the mass spectra of CV-ACSM. In addition, the differences between PM₁ and PM₂.₅ could be another explanation.

We then performed a linear regression on AMS O/C vs. CV-ACSM $f_{44}$ except for the conditions of RH < 20%, RH > 80%, OA > 70 μg m⁻³, and OA < 10 μg m⁻³ and obtained the following equation for estimation of O/C using CV-ACSM $f_{44}$:

$$\text{O/C} = 4.08 \times (\pm 0.03) \times f_{44} - 0.44 \times (\pm 0.01) \quad (1)$$

With this parameterization, we estimated the O/C of OA using CV-ACSM $f_{44}$ measurements during January–March in 2020. As shown in Fig. S14, the estimated O/C varied in the range of 0.19–0.79 with an average value of 0.58 (±0.10), which was overall higher than those in previous winters (0.37–0.56) (Sun et al., 2016; Xu et al., 2019). This is consistent with the decreased primary emissions and increased secondary OA in recent years (Lei et al., 2020; Sun et al., 2020) due to the clean air action since 2013. Therefore, the parameterization of O/C as a function of $f_{44}$ allows for a rapid estimation of O/C of OA from $f_{44}$ of CV-ACSM. This has a significant implication in studying the hygroscopicity of OA and CCN formation considering the rapidly increasing deployments of CV-ACSM worldwide.

4. Conclusions

The changes of size-resolved aerosol composition and sources of OA were characterized during a controlled CNY in Beijing. Our results showed considerable increases in secondary aerosol species except nitrate by 17.6–30.4% during the controlled CNY, yet the changes in SIA concentrations varied largely among different years due to the influences of meteorological conditions and precursors. Compared with previous CNY, the reductions in primary species were much smaller during the CNY of 2021, demonstrating the direct impacts of anthropogenic activities on primary aerosols. OA composition changed significantly during the CNY. The aqOOA decreased by 50% from BCNY to CNY, while OOA and OPOA increased by 34% and 176%, respectively. This result indicated the enhanced photochemical processing during the CNY consistent with the increased O/C from 0.53 to 0.59. The size distributions of aerosol species also changed, and the peak diameter of SOA shifted from 516 nm before CNY to 469 nm during the CNY. The analysis of a CNY haze episode showed a rapid transition of aerosol evolution from photochemical processing to aqueous-phase processing and wet scavenging, leading to significant changes in aerosol composition, size distributions, and OA composition. In addition, the parameterization relationship between AMS O/C and CV-ACSM $f_{44}$ was developed which has significant implications for characterization of oxidation degree and aging of OA, and evaluation of its impact on hygroscopicity and CCN formation considering the wide deployments of CV-ACSM worldwide.

Author statement

Weiqi Xu: Validation, Formal analysis, Investigation, Writing – original draft. Wei Zhou: Validation, Formal analysis, Investigation. Zhijie Li, Qingqing Wang, Aodong Du, Bo You, Lu Qi: Validation, Investigation. André S. H. Prévot, Junji Cao, Zifa Wang, Jiang Zhu: Writing – review & editing. Yele Sun: Conceptualization, Methodology, Funding acquisition, Writing – review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Fig. 4. OA concentration measured by CV-ACSM and RH dependence of the correlation, slope, and intercept for AMS O/C vs. CV-ACSM $f_{44}$. The data are grouped into grids with increments of RH and OA concentration being 20% and 10 μg m⁻³, respectively. The grids with the number of points less than five were excluded.
Data availability
Data will be made available on request.

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Appendix A: Supplementary data
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