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Impact of reduced anthropogenic emissions on chemical characteristics of urban aerosol by individual particle analysis

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1. Introduction

Increased attention recently has focused on aerosol particles because of their importance for air quality (An et al., 2019), human health (West et al., 2016), and global climate change (Twomey et al., 2021). To address severe air pollution problems and protect public health in China, a series of clean air policies has been established, such as the “Air Pollution Prevention and Control Action Plan” promulgated in 2013. Despite large reductions in primary emissions after the implementation of these controls (Feng et al., 2019; Zheng et al., 2018), the formation of secondary aerosols has continued to be a serious problem (He et al., 2017; Ma et al., 2017). On the other hand, strict short-term, local anthropogenic emission controls (such as those placed on traffic, catering, and industries) that were implemented for several international events (Li et al., 2016; Sun et al., 2016; Wang et al., 2010, 2016a; Zhao et al., 2017) have led improvements in air quality. For example, Shen et al. (2015) reported decreases (40–80%) in all target aerosol species during the 2014 Asia-Pacific Economic Cooperation (APEC) period. Meanwhile, Xu et al. (2015) reported that the contributions of secondary inorganic aerosol and organics were reduced by 62–69% and 35%, respectively, during that period, and the particle size distribution also shifted a small change in size from 650 nm to 400 nm. Shen et al. (2017) found that emission controls mainly influenced potassium-rich, organic and elemental carbon, and metal particles with diameters of 0.4–1.4 μm during the Second World Internet Conference held in Jiaxing, China.

These and other studies have shown that the effects of transport on the physicochemical characteristics of particles, source contributions, and spatial and temporal variations can become more apparent due to regional pollution controls, even for a short period. The evolution and formation mechanisms of air pollutants need to be further investigated to better understand how control measures can affect aerosol pollution.

In response to the rapid spread of the coronavirus 2019 disease (COVID-19), large-scale restrictions were placed on many outdoor human activities in China (including motor vehicle usage, catering, and industries) (Wang et al., 2020a). Due to large reductions of emissions during the COVID-19 lockdown period in China, both gaseous pollutants (e.g., nitrogen oxides (NOx) and sulfur dioxide (SO2)) and particulate matter (PM, including PM2.5 and PM10) showed clear decreases (Li et al., 2020a; Wang et al., 2020b; Zhao et al., 2020; Zheng et al., 2020). Nonetheless, haze events still occurred frequently in China during the COVID-19 lockdown.

Previous studies have related the occurrence of haze events to increases in the atmospheric oxidation capacity, which promotes the formation of secondary aerosols (Huang et al., 2021; Le et al., 2020; Sun et al., 2020). Unfavorable meteorological conditions have long been recognized as another factor that often contributes to air pollution events (Wang et al., 2020b). Indeed, complex interactions between chemistry, transport, and meteorology have made it difficult to quantify the contributions of primary emissions versus secondary particle formation to air quality. Highly time-resolved data for the characteristics of individual aerosol particles can provide important information relative to the effects and importance of the atmosphere aging processes.

The reactions and processes that drive the evolution of individual particles have been extensively investigated in urban areas. Some notable studies have shown that carbonaceous and the potassium-rich particles were the major particle types, each accounting for more than 30% of the total sources, whereas biomass burning, heavy metal, dust, and other particle types accounted for <15% (Li et al., 2014; Zhang et al., 2015). Other studies have shown that biomass burning, heavy metals, and dust particles have played important roles in specific pollution events (Chen et al., 2017; Ma et al., 2016; Dall’Osto et al., 2014). Fewer in-depth studies, however, have focused on secondary organic components (e.g., oxalic acid), metallic particles (e.g., Pb, Fe, etc.), and organic nitrogen compounds (e.g., imidazole, amine, etc.). Most of these components usually are in relatively low content, but they can have substantial effects on atmospheric reactions and human health (Zhou et al., 2020; Chen et al., 2018; Zhang et al., 2020). Generally, the formation of major secondary components (e.g., nitrate, sulfate and organics) suggests rapid condensation on existing particles during atmospheric aging (Khalizov et al., 2009; Zhang et al., 2013; Huang et al., 2019). Carbonaceous particles are more inclined to be internally mixed with sulfate than nitrate, while the opposite is true for inorganic particles (Zhang et al., 2015; Dall’Osto and Harrison, 2012). Aerosol mixing states can differ greatly with location in response to variations in chemical composition and secondary species (e.g., HSO4, NO3). These results highlight the differences in the behavior between carbonaceous versus inorganic particles in the atmosphere.

Relatively few studies of individual particles have been conducted during the large-scale COVID-19 lockdowns to date, but in one study, Li et al. (2020a) found that the numbers of carbonaceous particles decreased by 20.2% due to restrictions on industrial production and motor vehicle usage. Significant signal intensities of secondary inorganic ion fragments (SO2−4, NO2−, and HSO4−) were observed in all classes of particles at Liaocheng, an urban site in the North China Plain. Meng et al. (2021) investigated the impact of the COVID-19 lockdown on the formation of secondary organic aerosols (i.e., oxalic acid-containing particles) using a single-particle aerosol mass spectrometer (SPAMS), and these authors found that relative humidity (RH) promoted the conversion of precursors (e.g., glyoxal and methylglyoxal) to oxalic acid particles during the normal period. The ozone (O3) driven photochemical pathway also played an important role in the formation of oxalic acid particles under low RH, and the O3 concentrations increased remarkably during the COVID-19 lockdown period.

The Fenwei Plain was designated as a major pollution control region in China in 2018. As one of the eleven largest city clusters in the Fenwei Plain, Xianyang often suffers from severe air pollution, especially in winter. Indeed, over 57% of the days have been classified as polluted in fall and winter (i.e., October 2018 to March 2019); 43 days had extremely heavy pollution, and only 76 days had fine air-quality (http://www.scio.gov.cn/index.htm). The air quality of Xianyang has ranked low among the cities in China (http://www.mee.gov.cn, in Chinese). Source apportionments for Xianyang reported by Zhang (2018) showed that secondary species (26.5%) and vehicle exhaust (24.3%) were the two major contributors to PM2.5 pollution while those from coal combustions and biomass burning were 21% and 12% respectively in winter. Therefore, emissions from solid biofuels are of concern in the cold season.

Short-term air pollution control measures typically include restrictions on motor vehicle usage, closures of industries, etc. Studies of the composition, characteristics, and formation mechanisms of PM during restricted periods can provide insights into the causes of air pollution that would be helpful for developing efficient long-term control measures. In this study, the chemical composition and secondary formation of aerosols in Xianyang were investigated using an on-line SPAMS during the COVID-19 lockdown period. This study provides insights into the variations of chemical composition, size distribution, mixing state, and formation mechanism of aerosols in relation to changes in anthropogenic emissions at a heavily polluted city in China.
2. Methodology

2.1. Observation site

On-line measurements of aerosol size distributions and chemical composition were made from the rooftop of a 33-floor height building (distance to ground ~100 m) that was to the south of downtown Xianyang (34°18' N, 108°38' E, Fig. S1) from 1 January to February 18, 2020. The sampling site was in a new development zone and surrounded by residential and commercial areas; it was close to two expressways (G3023 and G344) and adjacent to the Liangsidu Park, which is to the southeast at a distance of ~2 km. There are some small industries around the site. Based on the run-up time of the Public Health Emergency Response Level I in Shaanxi Province, the sampling campaign was divided into two periods, the normal period (NP) from 1 to January 23, 2020 and the COVID-19 lockdown period (LP) from 24 January to February 18, 2020.

2.2. Measurements

A single-particle aerosol mass spectrometer (SPAMS, Model 0515, Hexin Analytical Instrument Co, Ltd, China) was used to continuously measure individual particles with aerodynamic sizes ranging from 0.2 to 2.0 μm. The flow rate for the SPAMS was 75 mL min⁻¹, and its operating principles have been discussed in detail elsewhere (Li et al., 2011; Wang et al., 2016b). In brief, after dried particles enter the SPAMS, they are immediately focused and accelerated to different velocities with the use of an aerodynamic lens. The aerodynamic diameters of the particles are then obtained through the use of two fixed distance (6 cm) continuous neodymium/yttrium aluminum garnet (Nd:YAG) diode lasers (532 nm) in the sizing region. The particles' chemical composition was determined using a desorption/ionization process with a pulsed 266 nm Nd:YAG laser. Counts for the generated positive and negative ion fragments were obtained along with the vacuum aerodynamic diameters.

A diagram of the SPAMS and the principles of the particle size calculations are presented in Fig. S2. Before the SPAMS analyses, the aerodynamic diameters and the mass-to-charge ratio (m/z) of positive and negative ion fragments were calibrated and optimized, respectively (Li et al., 2011). Contamination in the critical orifice was cleaned during the sampling periods, and the inlet pressure was controlled to within 2.40 ± 0.05 Torr. Further information on the SPAMS is provided in Supplemental Information Section 1.1.

2.3. Data acquisition

The YAADA 2.1 software (Allen, 2005), which is a MATLAB-based software toolkit (Version, 2014b, www.mathworks.com), was used to analyze the SPAMS achieved data. The mass spectra imported into YAADA were further processed using an adaptive resonance network (ART-2a) algorithm (Song and Hopke, 1999). For this study, the parameters for the ART-2a were set to a vigilance factor of 0.8, a learning rate of 0.05, and an iteration number of 20 for the data processing. A total of 1,839,083 mass spectra for 40,306,899 sized particles were acquired by SPAMS during the sampling campaign, and 9858 clusters were classified using the ART-2a algorithm.

The clusters were further merged into ten major groups, which accounted for 95% of total particles. Information on the composition of the ten groups is presented in Supplemental Information (Section 1.2). Information on the mixing states of the particles was obtained by evaluating the contributions of selected ion fragments to each particle type (Li et al., 2020b; Chen et al., 2016). The criteria used for searching the primary and secondary species in the SPAMS dataset are summarized in Table S2. The mixing states of the particle groups (not including “other” particles) that were classified as primary (based on levoglucosan and 35Cl⁻) and secondary (43CaH2O4, 48HC2O4, 97HSO4⁻, 46NO3⁻, and 18NH4+) were then compared between the NP and LP periods.

The mass concentrations of PM2.5 and gaseous species [i.e., nitrogen dioxide (NO2), sulfur dioxide (SO2), carbon monoxide (CO), and ozone (O3)], relative humidity (RH), temperature (T), wind direction (WD) and wind speed (WS) were obtained from the official data source of the Department of Ecology and Environment of Shaanxi Province (http://sthjt.shaanxi.gov.cn). The sampling site where those measurements were made was the national monitoring station at Liangsidu (Fig. S1), which is about 2 km from our SPAMS site. The average values for PM2.5, gaseous species, T and RH are shown in Table S1. Time-series plots of PM2.5, gaseous species and meteorological parameters are shown in Fig. S3, and the variations in these species and parameters are presented in Supplemental Information (Section 1.3).

3. Results and discussion

3.1. Variations of individual particles

The average particle number concentrations and the relative fractions of the particle groups are summarized in Table 1. The classification criteria for individual particles and the characteristic ion fragments for each particle type may be found in Supplemental Information Section 1.2. The ratios of the number of particles of a particular type to the total number of particles are presented as percentages.

During the NP, the largest hourly-averaged number fraction was for the NaK-SN group (42.4%), followed by EC-aged (31.5%), BB (12.1%), OC (5.3%), dust (2.3%), PAH-containing (2.2%), and OCEC (1.9%). The metal containing and EC-fresh particles have no further analysis—they relative percentages were low (<1%). The NaK-SN fraction was higher by 54.0% during the LP compared with the NP, and that can be attributed to the stronger oxidation during the LP because higher levels of oxidants favor the formation of secondary species. Reductions in traffic emissions during the LP can explain the decrease in the EC-aged fraction (23.7%). The BB fraction (12.6%), in contrast, was relatively consistent between the two periods. Dilution effects associated with changes in air masses between 14 and 18 February (Fig. S4c) are a likely reason why the mass concentration of PM2.5 decreased rapidly after 22:00 on 13 February. After that time, the number concentrations of NaK-SN and EC-aged particles decreased sharply (Fig. S5), while the number concentration of BB particles showed only minor changes. The PAH-containing particles showed an upward trend after the air masses changed, and that resulted in a higher fraction of PAH-containing particles (4.2%) during the LP compared with the NP.

Plots of diurnal variations show that increases in solar radiation were coincident with the formation of secondary species, and this can be seen as regular increases in the NaK-SN fraction from 08:00 to 15:00 local time (LT) during the NP (Fig. 1). The NaK-SN group showed minor changes after 16:00 LT, likely because aqueous-phase reactions contributed to the formation of secondary species when the radiative intensity decreased (Fig. S6). Different from the NP, a higher fraction of NaK-SN was seen at nighttime during the LP, suggesting that aqueous-phase reactions promoted secondary particle formation under high RH and O3 (Fig. S6). In contrast, decreases in the concentrations of the precursor NOx may have diminished the formation of secondary NaK-SN at 17:00 LT during the NP, even though concentrations of O3 were relatively high (Fig. S6). The EC-aged fraction showed similar temporal variations for both periods. That is EC-aged showed increases from 05:00 to 17:00 LT, and that can be ascribed to increases in traffic and motor vehicle emissions during the daytime despite the restrictions on motor vehicles during the LP.

The diurnal trends in the counts and relative fractions of BB, OC, PAH-containing, and OCEC particle were similar during the NP and LP, except for a peak in BB counts (Fig. S7) at 12:00 LT during the LP—this is a time when household cooking takes place and heating is active (Niu et al., 2016). As most people were confined at home during the LP, and there were no restrictions on biomass burning, the relative percentage of the BB fraction showed no obvious diurnal trends. The percent increases
3.2. Size distributions and mixing state

Secondary particles formation should be considered in the development of pollution control plans. This finding concerning oxidation capacity increased (Sun et al., 2020). This finding concerning 12.1% of the particles in the period. As shown in Fig. 2, NaK-SN ± decreased simultaneously 10.4%.

Restrictions on anthropogenic activities, did not eliminate air pollution. Variations in the EC-aged particle fraction were generally consistent with PM.

Clearly, the day-to-day changes in human activities and the increased relative percentages (Fig. 2b) in each particle group were similar. Variations in the EC-aged particle fraction were generally consistent with those from previous urban studies using the same instrument (Xu et al., 2019). Those from previous studies have shown that levoglucosan fragments (i.e., CHO2, C2H2O3, C2H3O2, C2H4O2, C2H5O2) are useful indicators of particles from biomass burning (Silva et al., 1999; Sullivan et al., 2007). During the NP, 69% of BB particles, 63% of PAH-containing particles, and 48% of OC particles contained levoglucosan fragments, and their proportions increased to 78%, 65%, and 64%, respectively, during the LP. The increases in the levoglucosan fractions of these particle groups may be explained by the fact that biomass-burning was not restricted during the LP. However, the increases also may have caused by the oxidation of organics during atmospheric aging (Zauscher et al., 2013; Zhang et al., 2019). Furthermore, it is noteworthy that the 35,37Cl− fragment, a possible primary indicator, which was mainly mixed with BB, OC and PAH-containing particles (19–29%). The other particle groups during both periods showed lower number fraction of 35,37Cl− (4–17%).

The 43C2H4O− and 89H2O2 ion fragments have been used as indicators of secondary formed organic species (Moffet et al., 2008). As shown in Figs. 4, 43C2H4O− had similar proportions in each particle group for both periods. Among all particle groups, the 43C2H4O− ion fragment was mainly associated with BB particles, and it had contributions of 31% and 26% during NP and LP, respectively. The OC particles were next most abundant group that had this ion fragment (14% and 18%), and that group was followed by OCEC particles (8% and 14%). The percent contributions of 13C2H4O− for the remaining particle groups were <9%.

Oxalate is another secondary species indicator, and the fractions of the 13C2H4O− ion fragments for each particle group were relatively low in the NP (3–15%) but increased by roughly two-fold (11–25%) during the

| Type       | Number count | Fraction in total (%) | Tracer ions |
|------------|--------------|-----------------------|-------------|
|            | Normal period | Lockdown period       | Normal period | Lockdown period |
| NaK-SN     | 243,131      | 202,101               | 42.2         | 54.0          |
| EC-aged    | 181,434      | 88,883                | 31.5         | 23.7          |
| EC-fresh   | 2944         | 1770                  | 0.5          | 0.5           |
| BB         | 69,932       | 47,051                | 12.1         | 12.6          |
| OC         | 30,741       | 6909                  | 5.3          | 1.8           |
| Dust       | 13,370       | 4020                  | 2.3          | 1.1           |
| PAH        | 12,455       | 15,553                | 2.2          | 4.2           |
| OCEC       | 10,738       | 2375                  | 1.9          | 0.6           |
| Metal      | 5574         | 1924                  | 1.0          | 0.5           |
| Others     | 5375         | 3978                  | 0.9          | 1.1           |

Abbreviations for particle types: NaK-SN: sodium, potassium, sulfate and nitrate; EC: elemental carbon; BB: biomass burning; OC: organic carbon; PAH: polycyclic aromatic hydrocarbon.

in the BB fraction at 16:00 LT was because there were lower concentrations of other anthropogenic pollutants (such as NaK-SN particles). Clearly, the day-to-day changes in human activities and the increased atmospheric oxidation capacity during the lockdown period had a great influence on both primary emissions and the chemical composition of PM.

The temporal trends in the number concentrations (Fig. 2a) and the relative percentages (Fig. 2b) in each particle group were similar. Variations in the EC-aged particle fraction were generally consistent with those of the PM2.5 mass concentration, while the NaK-SN fraction showed minor differences (Fig. 2b). For example, the PM2.5 concentration was elevated on 22 and 23 January and increased further on 24 to 26 January. Meanwhile, the relative fraction of EC-aged particles increased significantly (from 26.8% to 50.7%), while the NaK-SN showed only small fluctuations (54.3 ± 5.4%). The mass concentration of PM2.5 decreased sharply from 14 to 18 February, and the EC-aged fraction decreased simultaneously 10.4 ± 3.3%, while the NaK-SN fraction showed a smaller decreased and was the dominant particle group at 43.1 ± 12.1% of the particles in the period. As shown in Fig. 2, NaK-SN particle was the most abundant aerosol component in Xiangyan overall, and these particles are discussed in detail below.

An important finding of our study is that reductions in primary emissions, including those from coal combustion and traffic, due to the restrictions on anthropogenic activities, did not eliminate air pollution. In fact, the formation of secondary species increased as the atmospheric oxidation capacity increased (Sun et al., 2020). This finding concerning secondary particle formation should be considered in the development of pollution control plans.

3.2. Size distributions and mixing state

The number concentrations and number fractions of the size-resolved, particle groups during the two periods are illustrated in Fig. 3. The aerodynamic equivalent particle diameters were mainly in the range of 0.3–1.0 μm. In fact, aerosols in this size range accounted for 96% of the total detected particles. Our results are consistent with those from previous urban studies using the same instrument (Xu et al., 2019; G.H. Zhang et al., 2017). The maximum total particle number during the LP was for a particle diameter of 500 nm, while the corresponding value during the NP was 440 nm. This result shows that particle size generally increased during the LP.

Most of the nine particle types, that is the ten groups excluding “other” particle, showed maxima in their distributions at larger sizes during the LP compared with NP (Fig. 3a and b). In particular, the peaks in the distribution for the NaK-SN and dust particles shifted from 440 to 520 nm, and 460–540 nm, respectively, while the BB, OCEC, and PAH-containing particles increased from 440 to 500 nm. The size-resolved mixing states of secondary species and the above-mentioned particle types (dust, EC-aged, NaK-SN, BB, OC, PAH-containing particles) (Fig. S8) indicate that as the particle sizes increased, the proportions of HSO4−, NO3− and NH4+ in the dust, EC-aged, NaK-SN, and BB particles also increased. Moreover, the proportions of C2H2O− and oxalate in the NaK-SN, BB, OC, and PAH-containing particles increased as well. This is compelling evidence that the observed increases in particle size were associated with the enhanced formation of secondary species during the lockdown, and it is worth reiterating that during the LP, the atmospheric oxidizing capacity was higher than in the NP (Tian et al., 2021).

The size-resolved number fractions for the EC-aged and NaK-SN particles exhibited bimodal distributions during both the NP and LP (Fig. 3c and d). The smaller of the two particle size peaks presumably reflects the influences of direct emissions on the condensed particle mode (<300 nm), while the larger-sized peak was likely associated with secondary processes that affected the droplet mode (>400 nm). The number fractions of the size-resolved BB and OC particles showed similar distributions during the NP and LP, with peak values at ~480 and ~380 nm, respectively. Furthermore, the number percentage of the size-resolved PAH-containing particles with diameters >400 nm was higher during the LP than in the NP.

The mixing states (Fig. 4) of the particles were investigated by calculating the contributions of selected ion fragments (levoglucosan, 35,37Cl−, C2H4O−, C2H3O2−, C2H2O2−, C2H4O2−, and 14NH4+) to each particle type. Previous studies have shown that levoglucosan fragments (i.e., CHO2, C2H2O3, C2H3O2, C2H4O2, C2H5O2) are useful indicators of particles from biomass burning (Silva et al., 1999; Sullivan et al., 2007). During the NP, 69% of BB particles, 63% of PAH-containing particles, and 48% of OC particles contained levoglucosan fragments, and their proportions increased to 78%, 65%, and 64%, respectively, during the LP. The increases in the levoglucosan fractions of these particle groups may be explained by the fact that biomass-burning was not restricted during the LP. However, the increases also may have caused by the oxidation of organics during atmospheric aging (Zauscher et al., 2013; Zhang et al., 2019). Furthermore, it is noteworthy that the 35,37Cl− fragment, a possible primary indicator, which was mainly mixed with BB, OC and PAH-containing particles (19–29%). The other particle groups during both periods showed lower number fraction of 35,37Cl− (4–17%).
In terms of the particle groups, $^{89}\text{HC}_2\text{O}_4$ mainly was associated with the BB and PAH-containing particles during both periods. Lin et al. (2019) have shown that the main precursors of oxalate ($^{89}\text{HC}_2\text{O}_4$) include the following ion fragments: acetate ($^{59}\text{C}_2\text{H}_3\text{O}_2$), methylglyoxal ($^{71}\text{C}_3\text{H}_3\text{O}_2$), glyoxylate ($^{73}\text{C}_2\text{HO}_3$), pyruvate ($^{87}\text{C}_3\text{H}_3\text{O}_3$), malonate ($^{103}\text{C}_3\text{H}_3\text{O}_4$), and succinate ($^{117}\text{C}_4\text{H}_5\text{O}_4$). Due to the substantial amounts of these precursors emitted from biomass burning, oxalate probably formed on BB particles heterogeneously (Ervens et al., 2011). As discussed above, the PAH-containing particles also were influenced by the biomass burning, and that can explain why the oxalate ion...
Fig. 2. Time-series plots of (a) the number concentrations and (b) the relative percentages of ten particle groups and PM$_{2.5}$ mass concentrations during the study. The normal and lockdown periods are separated by yellow dashed lines. The solid, light blue line shows the PM$_{2.5}$ mass concentrations. Particle type abbreviations as in Table 1. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

Fig. 3. (a and b) Size distributions of the total number particle counts of nine particle types (excluding the “other” group) during the sampling campaign. Solid lines represent the normal period (NP) and the dash lines represent the lockdown period (LP); the relative percentages (%) of the total particles for nine groups during the (c) NP and (d) LP. Particle type abbreviations as above.
fragment also was associated with this particle group.

Nitrate ion fragments (\(\text{NO}_3^+\)) were more widely mixed with most of the particle types than the sulfate fragments (\(\text{HSO}_4^-\)) (Fig. 4), presumably due to the relative concentrations or reactivities of their precursors; that is, \(\text{NO}_2\) versus \(\text{SO}_2\) (Table S1). Except for the EC-fresh particles (<20%), \(\text{NO}_3^-\) had a fraction of >70% for all particle groups in both periods. In contrast, the ammonium ion fragment (\(\text{NH}_4^+\)) was a minor fraction of all particle groups (<4%), and the fraction of \(\text{HSO}_4^-\) was particularly high (>80%) for the organic particle groups (i.e., OCEC and OC particles). The particle mass spectra obtained from source emissions (see Section 1.4 of Supplementary Information) indicate that the strong signals for \(\text{NO}_3^-\) were caused by atmosphere aging. Therefore, these results are compelling evidence that most of the particle groups, except for the EC-fresh particles, had experienced a considerable degree of aging.

### 3.3. Secondary species formation

The \(^{43}\text{C}_2\text{H}_3\text{O}^+\), \(^{89}\text{HC}_2\text{O}_4^-\), \(^{62}\text{NO}_3^-\), \(^{97}\text{HSO}_4^-\), and \(^{18}\text{NH}_4^+\) ion fragments were used in our study to investigate the formation mechanism of secondary species (Chen et al., 2016). To characterize the impacts of the atmospheric oxidation and aqueous-phase reactions during the NP and LP, correlations were calculated for the number fractions of each secondary ion fragment versus the oxidant concentrations \((\text{O}_x = \text{O}_3 + \text{NO}_2)\).
As shown in Fig. 5a-d, when $O_3$ was <120 $\mu$g m$^{-3}$, the number fractions of $^{43}$C$_2$H$_4$O$^-$ ($R^2 = 0.11$) and $^{89}$HC$_2$O$_4^-$ ($R^2 = 0.44$) showed weak to modest correlations with $O_3$ during the NP but much higher correlations of 0.72 and 0.84, respectively, during the LP. Furthermore, the slopes of the linear regressions, with relative fraction as the dependent variable, were also higher during the LP, indicating stronger oxidant effects on the formation of secondary organic species during the lockdown. We note that when $O_3$ was >120 $\mu$g m$^{-3}$ during the LP, the number fractions of $^{43}$C$_2$H$_4$O$^-$ and $^{89}$HC$_2$O$_4^-$ decreased when $O_3$ increased. This inverse relationship can be attributed to the photolysis of $^{43}$C$_2$H$_4$O$^-$ and $^{89}$HC$_2$O$_4^-$ under high $O_3$ (>97 $\mu$g m$^{-3}$). A similar explanation has been proposed relative to the photodegradation of Fe-oxalate complexes in other studies (Huang et al., 2019; Zbou et al., 2020).

Furthermore, the high correlations between the precursor species (e.g., $^{45}$[HCO$_3^-$], $^{59}$[CH$_3$CO$_2^-$], $^{71}$[CH$_3$CO$_2^-$], $^{73}$[C$_2$H$_4$O$_2^-$], $^{87}$[C$_2$H$_4$O$_2$]) of oxalate and $O_3$ (Fig. S9) suggest that the decreased concentration of these precursors may limit oxalate formation.

The number fractions of $^{62}$NO$_3^-$ were positively correlated with $O_3$ during the NP ($R^2 = 0.84$, Fig. 5e-f), which implies that oxidation played an important role in aerosol nitrate formation. Interestingly, the correlation between the number fraction of $^{62}$NO$_3^-$ and $O_3$ was lower during the LP ($R^2 = 0.74$). Moreover, when $O_3$ was >70 $\mu$g m$^{-3}$, a higher slope was observed during the LP ($0.097$ m$^3$ $\mu$g$^{-1}$) compared with the NP ($0.08$ m$^3$ $\mu$g$^{-1}$), and this is further evidence that more oxidation occurred during the covid lockdown.

The percentages of $^{62}$NO$_3^-$ ion fragments decreased sharply (from 49% to 13%) from 16:00 13 February to 03:00 14 February, and during that time, the air mass trajectories to the site were from the northwest (Fig. S4c). Thus, the average value for the percentages of $^{62}$NO$_3^-$ ion fragments over this $O_3$ range (72.5 $\mu$g m$^{-3}$) reached 38%. When conditions were unfavorable for diffusion, $^{62}$NO$_3^-$ increased rapidly with $O_3$. For $^{97}$HSO$_4^-$, the correlations with $O_3$ were not significant for either the NP or LP dataset [Fig. 5g-h]. On the other hand, when $O_3$ was >70 $\mu$g m$^{-3}$, the correlations between the number fractions of $^{18}$NH$_4^+$ and $O_3$ were strong during both the NP ($R^2 = 0.91$) and LP ($R^2 = 0.81$) [Fig. 5i-j]. However, the number fraction of $^{18}$NH$_4^+$ remained stable when the $O_3$ was <70 $\mu$g m$^{-3}$ during both periods. The relatively high average value for $^{18}$NH$_4^+$ at $O_3$ <70 $\mu$g m$^{-3}$ was due to the high fractions (2.5%) observed during the NP from 11:00 3 January to 13:00 8 January. The high $^{18}$NH$_4^+$ may have been a consequence of high NO$_2$ and SO$_2$ because ammonium salts could produce through reactions initiated by these species.

For the secondary organic ion fragments [Fig. 6a-d], $^{43}$C$_2$H$_4$O$^-$ and $^{89}$HC$_2$O$_4^-$ showed strong negative correlations with RH during the NP ($R^2 = 0.72$ and $R^2 = 0.88$, respectively) and LP ($R^2 = 0.87$). Similar decreasing slopes for $^{43}$C$_2$H$_4$O$^-$ versus RH were found during the NP (<0.033) and LP (<0.038). In comparison, the slopes for $^{89}$HC$_2$O$_4^-$ obviously were much more negative when the RH increased (NP = −0.038; LP = −0.10). Previous studies have shown that $^{89}$HC$_2$O$_4^-$ mainly forms through heterogeneous reactions of precursor volatile organic compounds (VOCs) (Turekian et al., 2003; Kerminen et al., 2000), especially aqueous processes (Chen et al., 2015; Furukawa and Taka-hashi, 2011; J.K. Zhang et al., 2017). In addition, the organic precursors can polymerize to form more complex high molecular-weight products in humid environments (Carlton et al., 2007; Cheng et al., 2017; Tan et al., 2009).

As shown in Fig. 6e-j, the number fractions of $^{62}$NO$_3^-$ and $^{18}$NH$_4^+$ increased with the RH to some extent during both periods, indicating a critical role for aqueous-phase reactions in the formation of these species. Specifically, a higher correlation between the number fraction of $^{62}$NO$_3^-$ and RH was seen during LP ($R^2 = 0.76$) than NP ($R^2 = 0.54$) when RH was <60%, and the slopes of the regressions were both positive but quite different (0.080 and 0.57 during the NP and LP respectively). These results suggest that increases in humidity led to the production of $^{62}$NO$_3^-$. It also is worth noting that the average $O_3$ concentration was ~70% higher during the LP (77.0 $\mu$g m$^{-3}$) compared with the NP (45.1 $\mu$g m$^{-3}$). However, when RH was >60% during the LP, the number fractions of $^{62}$NO$_3^-$ tended to be stable, probably because the formation pathways were limited by low concentrations of precursor NO$_2$ (25.7 $\mu$g m$^{-3}$).

Strong positive correlations were found between the number...
fractions of $^{18}\text{NH}_3$ and RH, with $R^2$ values of 0.67 and 0.94 during NP and LP, respectively. In addition, similar slopes indicate comparable effects of aqueous-phase reactions leading to the formation of $^{18}\text{NH}_3$ during both periods. In contrast, $^{97}\text{H}_{2}\text{SO}_4$ showed inverse relationships with RH during NP ($R^2 = 0.29$) and LP ($R^2 = 0.50$). These findings are unlike those in other studies (Huang et al., 2021; Tian et al., 2019; Yue et al., 2019), and the disparate results could be related to the comparatively lower mass concentration of SO$_2$ (9.8 ± 4.2 μg m$^{-3}$) during the campaign at our site. In fact, several other field studies have not shown positive correlations between $^{97}\text{H}_{2}\text{SO}_4$ and RH under the low concentrations of SO$_2$ (<5 ppb) (Drewnick et al., 2006; Twyoh and Anderson, 2008; Schneider et al., 2017).

4. Conclusions

We compared and contrasted the chemical components, size distributions, mixing states of individual particles, and secondary particle formation for a normal period and the COVID-19 lockdown period using data obtained with a single particle aerosol mass spectrometer (SPAMS). Ten particle groups were identified, including NaK-SN, EC-aged, EC-fresh, BB, OC, dust, PAH-containing, OCEC, metal, and other particles during the study. The two largest particle number fractions showed positive correlations between $^{97}\text{H}_{2}\text{SO}_4$ and RH under the low concentrations of SO$_2$ (<5 ppb) (Drewnick et al., 2006; Twyoh and Anderson, 2008; Schneider et al., 2017). The strong mixing of these species is attributed to reduced anthropogenic emissions and increased in the NP and LP, respectively) and EC-aged particles (31.5% during the study. The two largest particle number fractions showed positive correlations between $^{97}\text{H}_{2}\text{SO}_4$ and RH under the low concentrations of SO$_2$ (<5 ppb) (Drewnick et al., 2006; Twyoh and Anderson, 2008; Schneider et al., 2017).

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.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.chemosphere.2022.135013.

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