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Influence of COVID-19 lockdown on the variation of organic aerosols: Insight into its molecular composition and oxidative potential

Wei Wang a,1, Yanhao Zhang a,1, Guodong Cao a, Yuanyuan Song a, Jing Zhang a, Ruijin Li b, Lifang Zhao b, Chuan Dong b, Zongwei Cai a,b

a State Key Laboratory of Environmental and Biological Analysis, Department of Chemistry, Hong Kong Baptist University, Hong Kong SAR, China
b Institute of Environmental Science, Shanxi University, Taiyuan, 030006, China

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ABSTRACT

To prevent the transmission of the novel coronavirus disease 2019 (COVID-19), China adopted nationwide lockdown measures on January 25, 2020, leading to an evident diminution in the observed air pollutants. To investigate the influence of the lockdown on atmospheric chemistry, the specific molecular composition, oxidative potential of organic aerosols (OAs) in PM$_{2.5}$ were studied using a high-resolution orbitrap mass spectrometry at a typical coal-combustion city, Linfen, in the North China Plain (NCP). The major air pollutants including PM$_{2.5}$, PM$_{10}$, SO$_2$, NO$_2$, and CO were observed to be diminished by 28.6–45.4%, while O$_3$ was augmented by 52.5% during the lockdown compared to those before the lockdown. A significant decrease of oxygen-containing (CHO) compounds (24.7%) associated with anthropogenic acids was observed during the lockdown, implying a reduction in fossil fuel combustion. The coal-burning related sulfur-containing organo-sulfates (CHOS-) and nitrooxy-sulfates (CHONS-) have also shown attenuated in both their relative abundances and anthropogenic/biogenic ratios. Amine/amide-like CHON $+$ components have decreased by 27.6%, while nitro/nitrooxy-containing CHON- compounds have only decreased by 7.1%. Multi-source nitrogen-containing (CHN) compounds have shown a moderate elimination of 24.0%, while the identified high-condensed azarenes have fallen from 17.7% to 14.7%, implying a potential reduction in the health risk of OAs during quarantine. The measurement of OAs’ oxidative potential through dithiothreitol (DTT) assay has confirmed that as it had dropped from 0.88 nmol min$^{-1} \cdot m^{-3}$ to 0.80 nmol min$^{-1} \cdot m^{-3}$. High correlations were observed between the abundance of OA subgroups with the concentration of PM$_{2.5}$ after the execution of the lockdown, suggesting a potential elevation in the contribution of organic components to the total PM$_{2.5}$ level. Our study provides insightful compositional and health-related information in the variation of OAs during the lockdown period and attests to the validity of joint-control strategy in controlling the level and health risks of numerous atmospheric pollutants.

1. Introduction

After the outbreak of Coronavirus disease 2019 (COVID-19) in China, a series of lockdown measures were rapidly implemented by the government to prevent the transmission of the virus. These measures include compulsory isolation, closing nonessential public facilities, restricting transportation and contacts. As a result, anthropogenic activities like industrial production and vehicle emission were highly reduced, and the level of air pollutants was observed to plummet correspondingly (Chen et al., 2020b; Chu et al., 2021). These lockdown measures were firstly conducted on January 23 in Wuhan, Hubei province where this novel pneumonia-like disease was firstly reported (Zheng et al., 2020). On January 25, the Chinese government launched the highest level of public health emergency response in 31 provinces in mainland China (Tu et al., 2020). During this period, it is not only observed the decreases in the absolute concentration of ambient fine particulate matter (PM$_{2.5}$, particles with aerodynamic diameter $\leq 2.5$ μm) and other air pollutants, their emission sources, chemical composition and related health effects could also be influenced. The COVID-19 epidemic has provided a valuable opportunity to investigate the significance of controlling societal production and human activities on the mitigation of air pollution.

* Corresponding author.
E-mail address: zwcai@hkbu.edu.hk (Z. Cai).
1 These authors contributed equally to this work.

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Several studies have investigated the change in the chemical composition of PM\(_{2.5}\) before and during the lockdown. Chu et al. (2021) have found a significant concurrent reduction in PM\(_{2.5}\) (19% in China excluding Hubei) and NO\(_2\) (30% in China excluding Hubei) levels during the epidemic and support that controlling the level of NO\(_x\) can further reduce PM\(_{2.5}\) pollution in China. Cui et al. (2020) have investigated the composition and source of PM\(_{2.5}\) at a rural site between Beijing and Tianjin, finding a considerable reduction from dust, coal combustion and industrial production. Chen et al. (2020a) have studied the variation of OAs in their molecular composition and oxidative potential during the lockdown period. To obtain a more specific and comprehensive understanding of the influence of lockdown measures on the control of atmospheric pollutants during the epidemic, an intensive formation of secondary aerosol was observed due to the increased level of oxidant in Shanghai, leading to haze periods during the epidemic. Zheng et al. (2020) have assessed the chemical composition, source contribution of PM\(_{2.5}\) in Wuhan, the first city that adopted the lockdown measures, revealing an overall increase of PM\(_{2.5}\) species ranging from 0.85 \(\mu\)g m\(^{-3}\) (chloride) to 9.86 \(\mu\)g m\(^{-3}\) (nitrate) mainly from the suspension of industrial activities. These studies mainly focused on the macroscopic level of chemical species (e.g., organic carbon, elemental carbon, trace element) or inorganic aerosols (e.g., nitrate, ammonium, chloride, sulfate). Characterization of the organic fraction (as known as organic aerosol, OA) of PM\(_{2.5}\) at the molecular level, however, was rarely reported. Related health effects like oxidative potential (OP) were also ambiguous due to the research gap. To obtain a more specific and comprehensive understanding of the influence of lockdown measures on the control of atmospheric pollutants during the epidemic, an intensive study on the variation of OAs in their molecular composition and oxidative potential is necessary.

In this study, 24 h of PM\(_{2.5}\) samples were collected in a typical northern coal combustion city, Linfen, to study the influence of lockdown on the molecular composition and oxidative potential of OA. Two periods were selected in this study including before (January 1 to 24) and during the lockdown of the city (January 29 to February 9). High-resolution orbitrap mass spectrometry was used to characterize the specific molecular composition of OAs during these two periods. The oxidative potentials of the extracted OA components were ascertained by the dithiothreitol (DTT) assay. Correlation between the concentration of PM\(_{2.5}\) and the molecular composition of OAs as well as its oxidative potential was also further discussed in this study to find out their potential relationships.

2. Materials and methods

2.1. Sample collection and pretreatment

PM\(_{2.5}\) samples collection were conducted using quartz microfiber filters (QMA, 90 mm, Whatman International Ltd, UK) with a medium volume air sampler (ADS-2062E, AMAE (Shenzhen) Co., Ltd, China) for 24 h (~140 m\(^3\) total volume) from January 1 to February 9, 2020. The sampling site was located at Mingjiang Town, Hongdong County, Linfen, Shannxi Province (36°20’N, 111°22’E). The quartz filters used in this study were baked at 550\(\degree\)C for 5 h in advance to eliminate possible contaminants. After sampling, all the filters were wrapped with aluminum foil and stored at a -80\(\degree\)C freezer for further analysis.

The extraction procedure was performed with reference to earlier studies with modification (Wang et al., 2018). Briefly, a 4 cm\(^2\) portion of the filter was cut into a tube, adding 2 mL acetonitrile-water (8/2, v/v) as the extraction solvent. Then the sample was extracted 3 times in an ultrasonic bath for 30 min. After pouring these extracts together, the mixture was filtered through a 0.22-\(\mu\)m Teflon syringe filter and blown with purified nitrogen gently to near dryness. Finally, the residual was redissolved in 1 mL acetonitrile-water (1/9, v/v) solvent for subsequent determination.

2.2. UHRMS analysis

Sample analysis was carried out with an ultrahigh-resolution mass spectrometer (Q Exactive Hybrid Quadrupole-Orbitrap Mass Spectrometer; Thermo Scientific, USA) coupled to an UHPLC system (Dionex UltiMate 3000, Thermo Scientific, USA). Analytes were separated using a Waters Acquity BEH C18 column (1.7 \(\mu\)m, 2.1 \(\times\) 100 mm) with mobile phases consisting of (A) 2% acetonitrile and 0.04% formic acid in ultrapure water and (B) 2% ultrapure water in acetonitrile. Elution procedure was used in the gradient mode with a flow rate of 300 \(\mu\)L/min and the following gradients: start with 2% B for 1.5 min and firstly increased linearly to 20% B in 1 min and held for 5 min, then increased linearly to 98% B in 1 min and held for 2.5 min, back to 2% B in the next 5 min and hold for 1 min. The injection volume of each sample was 20 \(\mu\)L and blank filter samples were also analyzed for background subtraction.

The spray voltage of the ESI source equipped for Q-Exact mass spectrometer (V4.3.7, Thermo Scientific, USA) to subtract the blank sample for the elimination of background peaks from contaminants and other interferences. Then the data were processed by MZmine (V2.53) software, which enables several LC-MS data processing functions (Lin et al., 2012; Pluskal et al., 2010; Tao et al., 2014; Wang et al., 2017). The processing workflow and parameters were set with reference to previous studies and were described in the supporting information (Wang et al., 2017, 2020b). It should be noted that the compositional elemental of these formulas was constrained as C\(_{4-8}\)H\(_{20-100}\)O\(_{0-3}\)-N\(_{0-3}\)-S\(_{0-3}\)-P\(_{0-3}\)-F\(_{0-3}\)-Cl\(_{0-3}\)-Br\(_{0-3}\). and that m/z tolerance was 3 ppm for both ESI modes. Several indicators were adopted to illustrate the characters of OA subgroups including double bond equivalent (DBE), modified aromaticity index (A\(_{\text{mod}}\)), aromaticity equivalent (Xc) and Kendrick mass defect (KMD). Their specific calculation was presented in the supporting information.

2.4. DTT assay

The oxidative potential of the extracted PM\(_{2.5}\) samples was evaluated by the DTT assay in reference to the study of Ma et al. (2018) with a slight modification. Briefly, 20 \(\mu\)L of each extracted and filtered sample in the solution of acetonitrile-water (1/9, v/v) were dispensed into a 1.5 mL tube. 920 \(\mu\)L of potassium phosphate buffer (pH = 7.4) and 50 \(\mu\)L of 0.5 mM DTT were added into the tube successively. The tube was then placed into a shaker with the temperature-controlled at 37\(\degree\)C (simulating the human environment), shaking for 90 min to ensure a better correlation between DTT consumption and reaction time. After spiking 100 \(\mu\)L of 1.0 mM 5,5’-dithiobis-2-nitrobenzoic acid (DTNB) into the mixture, the residual DTT was quantified immediately by measuring its light absorbance at 412 nm using an ultraviolet-visible (UV-Vis) spectrophotometer (Hewlett, CA, USA). The DTT consumption of each extracted PM\(_{2.5}\) sample was blank corrected and then normalized by the volume of air sampled (DTT\(_V\), in units of nmol-min\(^{-1}\) m\(^{-3}\)) with the following equation:

\[
\text{DTT}(\%) = \frac{R_{\text{DTT}}(\%)}{n_{\text{DTT}}(\text{nmol})} \times \frac{\text{Air volume}}{(\text{min})} (1)
\]

where \(R_{\text{DTT}}(\%)\) is the consumption of DTT in percentage, \(n_{\text{DTT}}(\text{nmol})\) is the total amount of DTT that added, \((\text{min})\) is the reaction time, and
Air volume ($m^3$) is the corresponding sampling volume of filters used.

2.5. Statistical analysis

The Pearson correlation analysis and the multiple linear regression model were carried out in the corresponding statistical analyses. A $p$ value less than 0.05 was considered statistically significant. All the statistics were implemented using the Statistical Program for Social Sciences (SPSS, Version 11.0, IBM, SPSS Inc.).

3. Result and discussion

3.1. Changes in the level of major air pollutants

Similar to those in other cities in China, the air pollutants in Linfen also showed a downward trend during the lockdown. Fig. 1 showed the temporal variations in the concentration of major air pollutants and their variation rates. It is clear that the mean concentrations of PM$_{2.5}$, PM$_{10}$, NO$_2$, SO$_2$ and CO have decreased by 28.57%, 35.85%, 45.39%, 35.20%, 38.58% respectively, while that of O$_3$ increased by 52.49%. The amplitude of the variation was greater than the national mean change rates of PM$_{2.5}$ (-20.1%), PM$_{10}$ (-15.0%), O$_3$ (21.9%), NO$_2$ (-35.7%), SO$_2$ (-20.1%) and CO (-13.0%), indicating a strong influence of the lockdown measures on the alleviation of air pollution in Linfen (Zheng et al., 2020). Among all these 6 kinds of pollutants, it is only ozone (O$_3$) that showed a conversely upward trend after the implementation of quarantine measures. The ascent of O$_3$ could be attributed to the increase in its production rate, as the reduction of PM$_{2.5}$ could impair its role as a scavenger of hydroperoxyl and NO$_x$ radicals that would otherwise produce ozone (Dang and Liao, 2019; Li et al., 2019a, 2019b). A similarly elevated ozone level was also observed in other cities and areas like Wuhan, Shanghai, Barcelona, Baghdad, and eastern India during the lockdown period (Chen et al., 2020a; Hashim et al., 2021; Sharma et al., 2020; Tobias et al., 2020; Zheng et al., 2020). A higher decrease rate of PM$_{10}$ than that of PM$_{2.5}$ was observed, indicating a strong reduction of primary aerosol compared to the secondary aerosol as the former showed a higher contribution to PM$_{10}$ than PM$_{2.5}$ (Seinfeld and Pandis, 2016). A significant decrease of CO ($p < 0.01$) also verified

![Graph showing the concentration of PM$_{2.5}$, PM$_{10}$, NO$_2$, SO$_2$, O$_3$ and CO in Linfen during the measurement periods (a) and their variation in absolute value and percentage (b). The light orange and light green shaded areas represent two periods: before and during the lockdown period. Different numbers of * represent different significant levels: *$p < 0.05$, **$p < 0.01$, ***$p < 0.001$. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)](image-url)
this result as CO is often used as a marker of primary emission considering its relatively long lifetime against oxidation by OH radicals (DeCarlo et al., 2010). A remarkable decrease of NO$_2$ (p < 0.001) was observed, with its mean concentration declining from 59.10 ± 14.36 to 32.27 ± 6.73 μg m$^{-3}$, which may be related to the marked drop in traffic intensity (Wang et al., 2020a). A concurrent decrease in PM$_{2.5}$ and NO$_2$ during the Covid-19 epidemic was revealed regarding their temporal and spatial variations in China, implying the potential effectiveness of controlling NO$_2$ in reducing PM$_{2.5}$ pollution (Chu et al., 2021). Similarly, the level of SO$_2$ also showed to decrease by 35.20% during the lockdown period. As an important indicator of coal combustion, the shrink of SO$_2$ may imply a potential reduction of coal-burning under the COVID-19 epidemic control measures. However, considering that coal combustion is the basic energy supply for electricity and central heating and contributed 57.7% to the total energy supply in China during 2019, the (DBE) and modified aromaticity index (AI) of each subgroup in PM$_{2.5}$ before and during quarantine. Former studies have found that most of the CHO compounds consisted of carboxylic acids, oxygenated polycyclic aromatic hydrocarbons containing deprotonatable carbonyl, carboxyl functional groups, which tend to occur preferentially in negative ionization mode (Lin et al., 2012, 2016). The CHO compounds should be discussed separately as most of the CHO compounds showed an O/N ratio lower than 3, which were assigned to have reduced nitrogen-containing functional groups like amines, while 71% of the CHO + compounds showed an O/N ratio higher than 3, which may associate with nitro (-NO$_2$) or nitroxy (-ONO$_2$) groups in these formulas (Mo et al., 2018; Wang et al., 2018). Most of the CHOS- (87%–92%) compounds and CHONS- (66%–78%) compounds showed O/S ≥ 4 or O/N ≥ 4, indicating a potential sulfonic acid group (-OSO$_2$H) and/or nitric acid group (-ONO$_2$) (O’Brien et al., 2013). Considering that, these molecules could be potentially identified as organosulfates (OSs) or nitrooxy-organosulfates (Wang et al., 2017).

Fig. 2(a) showed the temporal change of the abundance for each subgroup and their proportion in percentage. An evident decreasing tendency for each subgroup was identified during the lockdown period, which is consistent with the variation of PM$_{2.5}$. Fig. 2(b) showed the variation of each subgroup in absolute abundance and percentage. It can clearly be seen that all the subgroups showed a declining tendency in both ESI+ and ESI- after the execution of the lockdown measures. However, the changing rates for each subgroup vary from ~7.09% to ~31.95%. As a basic component of the oxygenated organic aerosol, CHO compounds have a mean decreasing rate of 24.73%. Among these oxygenated molecules, organic acid was a good indicator reflecting the source of secondary organic aerosols (SOAs) (Chan et al., 2011; Nozière et al., 2010). By identifying the potential composition, organic acids could be used to illustrate the source of SOAs from anthropogenic or biogenic origins. Figure S2 showed the relative intensity (RI) of identified organic acids derived from the anthropogenic/biogenic source and the ratios of adipic acid to azelaic acid (C$_9$/C$_{11}$) and phthalic acid to azelaic acid (Ph/C$_{11}$) respectively. These ratios have been widely adopted to reflect the relative contributions of anthropogenic versus biogenic SOAs (Hansen et al., 2014; Yu et al., 2021). By comparison, it is clear that both the abundance of identified acids and the anthropogenic/biogenic source ratios decreased during the lockdown period, indicating the reduction of acidic anthropogenic source SOAs. Meng et al. (2021) have investigated the impact of lockdown on the level and source of oxalic

### Table 1

| Period       | Elemental composition | Number of formulas | MW   | O/C  | H/C  | DBE | Al$_{mod}$ |
|--------------|-----------------------|--------------------|------|------|------|------|------------|
| **Before lockdown** |                       |                    |      |      |      |      |            |
| CHO+         | 1537                  | 288.72             | 0.30 | 1.07 | 8.89 | 0.42 |
| CHON+        | 2465                  | 281.11             | 0.29 | 1.23 | 8.93 | 0.40 |
| CHONS+       | 1007                  | 317.18             | 0.61 | 1.40 | 6.40 | 0.21 |
| CHOS+        | 171                   | 210.50             | 0.24 | 1.22 | 6.01 | 0.34 |
| CHN+         | 357                   | 199.70             | 0.00 | 1.22 | 7.42 | 0.52 |
| CHO          | 1489                  | 326.59             | 0.35 | 1.13 | 9.26 | 0.43 |
| CHON         | 1371                  | 296.49             | 0.35 | 1.04 | 9.46 | 0.63 |
| CHONS        | 1307                  | 345.78             | 0.67 | 1.45 | 6.74 | 0.24 |
| CHOS         | 743                   | 323.12             | 0.65 | 1.14 | 7.75 | 0.36 |
| **During lockdown** |                       |                    |      |      |      |      |            |
| CHO+         | 1419                  | 285.91             | 0.30 | 1.02 | 9.21 | 0.45 |
| CHON+        | 2428                  | 283.53             | 0.29 | 1.22 | 8.71 | 0.41 |
| CHONS+       | 949                   | 315.86             | 0.62 | 1.58 | 5.93 | 0.19 |
| CHOS+        | 187                   | 213.32             | 0.24 | 1.24 | 6.15 | 0.34 |
| CHN+         | 384                   | 192.82             | 0.00 | 1.23 | 7.00 | 0.51 |
| CHO          | 1560                  | 323.71             | 0.37 | 1.12 | 9.53 | 0.43 |
| CHON         | 1541                  | 299.91             | 0.35 | 1.06 | 9.33 | 0.32 |
| CHONS        | 1373                  | 348.61             | 0.67 | 1.45 | 6.14 | 0.24 |
| CHOS         | 688                   | 310.88             | 0.69 | 1.22 | 6.51 | 0.31 |
acid, revealing a 29% decrease of biomass burning related oxalic acid during the lockdown.

The CHON + compounds may represent a large proportion of oxidized amines/amides with relatively higher AI (mod) or DBE value and lower O/N ratio (<3) (Wang et al., 2017), while the CHON- molecules were mainly organonitrates with higher O/N (≥3) (Wu et al., 2019). A significant decrease of CHON + compounds (27.57%, p < 0.01) may imply a large reduction of amine/amide-like substances, which could be associated with the reduction of direct emissions of industrial and tobacco smoke (Ge et al., 2011). Different from CHON + compounds and other subgroups, CHON- molecules showed a lower decreasing rate of only 7.09%, making its relative proportion increase by 3.4% (pie chart in Fig. 2 (a)). This may be related to the weaker nitrate radical chemistry caused by the reduction of NOx, and a similar change was also observed during the 2014 Asia-Pacific Economic Cooperation (APEC) summit period (Mo et al., 2018).

The CHOS (organosulfates) and CHONS (nitrooxy-organosulfates) molecules were tended to be ionized in negative ESI+, leading to a lower percentage in ESI+ (~10%) and a high percentage in ESI- (~40%) among all the molecules. Earlier studies have proven that they are formed from acid-catalyzed and/or NO3-initiated oxidation reactions that are related to the combustion of fossil fuel (especially coal) or biogenetic sources (Cai et al., 2020). As a result, the remarkable decrease of NO2 and SO2 (Fig. 1) may be highly correlated to the reduction of OAs, understanding their specific variation in molecule level was also crucial. Fig. 3 showed the Van Krevelen (VK) diagram of OA molecules that were lost/decreased (b) after the implementation of the lockdown measures. By constructing the VK diagram with the H/C and O/C of each molecule, one can get the categorical distribution of each subgroup. In ESI+, most of the eliminated molecules were sulfur-containing CHOS and CHONS compounds, accounting for 65% of the total number of molecules. As described above, these molecules were mainly composed of OAs or nitrooxy-OAs that were highly related to the combustion of fossil fuel. The vast reduction of these compounds, therefore, may imply a potential deduction of fossil fuel combustion. Besides that, these S-containing molecules were mainly distributed in the range of O/C 0.25–0.75, H/C 0.3–1.2, similar to the range that was recognized as the unique coal-combustion-produced molecules located in the area of O/C 0–0.6, H/C 0.3–1.0 (Tang et al., 2020). These results have further verified that the lost molecules obtained from ESI- were mainly caused
by the reduction of coal combustion. An extensive loss of CHONS compounds (27.7%) was also noticed in ESI+, showing a broad distribution compared to other species. Considering the remarkable decrease of their DBE and Al_mod level (Table 1), these molecules could be attributed to aromatics-containing reduced sulfur that is originated from fossil fuel combustion as reported in Shanghai and Wilmington (Mead et al., 2015; Wang et al., 2017). The decreased/lost CHON + molecules mainly concentrated in the low-oxidized area with an O/C less than 0.5, indicating that they were CHON + compounds containing more condensed nitrogen atoms, which could be produced from a minor pyrolytic and oxidative processing (e.g., smoldering burning) of N-heterocycle compounds (e.g., imidazole) (Lin et al., 2012). The decrease of these molecules implied a potential diminution of biomass burning during the quarantine period. Similar to CHON + compounds, most of the disappeared CHO + compounds (~79%) also showed an O/C less than 0.5 and could be considered as low oxidated aliphatic/aromatic compounds (Wang et al., 2018). Wang et al. (2017) have investigated the molecular composition of OAs in Shanghai and suggested that the CHO + molecules were likely to be associated with the direct emission of biomass burning. A reduction of these compounds may suggest the mitigation of biomass burning during quarantine. As there is no oxygen atom in the CHN compounds, the variation of CHN molecules was shown separately in Figure S5. Compared to those molecules before lockdown, which shows a relatively higher DBE (7.42), the CHN compounds during lockdown were observed to be more saturated (DBE = 7.00). The fraction of naphthalene/anthracene/pyrene-core structural aromatic CHN molecules has decreased from 56.6% to 42.9%. CHN compounds with 12–23 DBE and 15–29 carbon atoms were regarded as highly condensed azarenes molecules (above the dashed line in Figure S5), which were reported to have strong mutagenesis and potentially carcinogenic (Wang et al., 2018), having decreased from 17.7% to 14.7% after the implementation of lockdown measures. As the markers of coal combustion, the decrease of condensed azarenes verified the reduction of coal-burning and may further indicate a potential decline in the health risk of PM2.5 during the quarantine period (Alves et al., 2017; Bandowe et al., 2016).

3.3. Oxidative potential and correlations

To better understand the change in the health risk of OAs, together with the relationships between that with their molecular composition, the oxidative potential (OP) of the extracted components were also evaluated. The OP represents the ability of particular matters to generate reactive oxygen species (ROS), which has been suggested as a key mechanism underlying the toxic effects of exposure to OAs (Delfino et al., 2011; Esposito et al., 2014). A variety of methods were developed to evaluate the OP of particular matters, and the DTT assay was most adopted due to its high sensitivity to a variety of PM components (e.g., quinones, transition metals and HULICs) (Bates et al., 2019; ChARRIER and Anastasio, 2012; Verma et al., 2015). In this study, the DTT assay was used to evaluate the OP of OAs before and during lockdown periods in order to investigate the correlation of that with the molecular compositional subgroups of OAs.

Table 2 summarized the Pearson correlation coefficients of the abundance for each subgroup with the concentration of gaseous pollutants and DTT. It could be seen that all the species showed an amplified correlation to the content of PM2.5 during the lockdown period in comparison with that before the lockdown. Considering the enhanced secondary formation of OAs associated with the increased O3 level, this result may imply a potential increase in the contribution of organic components to the total concentration of PM2.5. A similar increased share of organic carbon was also observed in Wuhan and Shanghai (Chen et al., 2020a; Gu et al., 2021; Zheng et al., 2020). Among all these organic subgroups, significant positive correlations were found between CHONS- (p = 0.700) and the concentration of PM2.5 as well as between CHO- and PM2.5 during quarantine, which was much higher than that before the quarantine. As a tracer of secondary formatted OAs, OOs and nitrooxy-OSs originated from the oxidation of biogenic VOCs (e.g., isoprene and α-/β-pinene) as well as anthropogenic PAHs (Ning et al., 2019). The increment in their correlation coefficients may imply an elevated contribution of SOAs to the total concentration of PM2.5 due to the enhanced atmospheric oxidizing capacity. High associations of the level of ozone with CHONS- (p = 0.847, r < 0.05) and with CHO- (p = 0.935, r < 0.01) also verified the boosted OOs and nitrooxy-OSs levels due to the increase of O3 during the lockdown. A former study also signified the enhanced photochemical formation of secondary SOAs during the COVID-19 lockdown in northern China (Meng et al., 2021). As mentioned before, PM10 and CO were more sensitive to the POAs (DeCarlo et al., 2010; Seinfeld and Pandis, 2016). A relatively higher association of the organic species with the level of PM10 and CO than that with PM2.5 may indicate a higher level of direct emission caused by human activities before lockdown.

Similar to the interaction between the species abundance and the concentration of PM2.5, an increased relevance between these OA subgroups in PM2.5 with its oxidative potential could also be ascertained from Table 2, highlighting their determining role in the oxidative potential of PM2.5 during the lockdown. It is usually accepted that the DTT,

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**Fig. 3.** Van Krevelen diagram of OA molecules obtained from ESI- (left) and ESI+ (right) that were lost/decreased after the implementation of lockdown measures. Different subgroups were shown by different colors and shapes. The pie chart represents the number proportion of each subgroup. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)
The assay is highly sensitive to both organic species and transition metals in PM$_{2.5}$ (Fang et al., 2016). It is proposed that the reduction of human activity could mitigate the level of metal elements in the atmospheric environment, thus emphasizing the organic carbon-related ROS production during the lockdown period (Cui et al., 2020). As shown in Table 2, among the organic species, it is molecules appertained to CHO$^+$ ($r = 0.950, p < 0.001$) and CHON$^-$ ($r = 0.921, p < 0.01$) groups that showed the two highest correlations with the DTT activities. Fig. 4 showed the temporal variation in the abundance of these two subgroups, DTT activities, and their linear correlations. A significant linear association was found between the abundance of CHO$^+$ and CHOS$^-$ with the level of DTT activity during the lockdown, suggesting that these two components may play a vital role in the formation of the oxidative potential of PM$_{2.5}$ in that period. Many previous studies also found high correlations between the organic species of PM$_{2.5}$, especially water-soluble organic carbon (WSOC), with its oxidative potential.

|          | Before lockdown | 0.325 | −0.006 | 0.368 | −0.534* | −0.292 | 0.131 | 0.217 | 0.453 | 0.568* |
|----------|-----------------|-------|--------|-------|---------|--------|-------|-------|-------|--------|
|          | During lockdown | 0.388 | 0.637  | 0.510 | 0.009  | 0.330  | 0.432 | 0.371 | 0.700 | 0.825* |
|          | Total           | 0.420 | 0.217  | 0.420 | −0.399 | −0.071 | 0.288 | 0.259 | 0.551** | 0.609** |
|          | CHON$^+$        | 0.329 | 0.028  | 0.364 | −0.514* | −0.265 | 0.159 | 0.243 | 0.456 | 0.541* |
|          | CHOS$^+$        | 0.273 | 0.644  | 0.474 | 0.043  | 0.358  | 0.413 | 0.383 | 0.672 | 0.779  |
|          | Total           | 0.451* | 0.286  | 0.416 | −0.343 | −0.004 | 0.344 | 0.328 | 0.580** | 0.591** |
|          | CHOs$^-$        | 0.132 | −0.123 | 0.018 | 0.244  | −0.067 | 0.195 | 0.353 | 0.044 | 0.283  |
|          | CHN$^+$         | 0.772 | 0.921** | 0.860* | 0.427  | 0.727  | 0.805 | 0.668 | 0.935** | 0.845* |
|          | Total           | 0.081 | −0.115 | 0.111 | 0.138  | −0.056 | 0.107 | 0.342 | −0.004 | 0.172  |
| NO$_2$   | Before lockdown | 0.148 | 0.231  | 0.216 | −0.293 | 0.121  | 0.014 | −0.047 | 0.032 | −0.195 |
|          | During lockdown | 0.505 | 0.549  | 0.664 | 0.131  | 0.301  | 0.640 | 0.509 | 0.584 | 0.603  |
|          | Total           | 0.421 | 0.504  | 0.323 | −0.124 | 0.348  | 0.365 | 0.092 | 0.375 | 0.073  |
| SO$_2$   | Before lockdown | 0.464 | 0.321  | 0.515* | −0.393 | 0.192  | 0.296 | 0.398 | 0.241 | 0.211  |
|          | During lockdown | 0.463 | 0.342  | 0.485 | 0.464  | 0.403  | 0.557 | 0.474 | 0.237 | 0.009  |
|          | Total           | 0.553** | 0.452* | 0.537** | −0.207 | 0.340  | 0.460* | 0.422 | 0.377 | 0.271  |
| CO       | Before lockdown | 0.547* | 0.161  | 0.674** | −0.711** | −0.090 | 0.228 | 0.263 | 0.356 | 0.401  |
|          | During lockdown | −0.016 | −0.070 | 0.153 | −0.766 | −0.498 | 0.078 | 0.017 | 0.179 | 0.570  |
|          | Total           | 0.577** | 0.372  | 0.594** | −0.453* | 0.098  | 0.403 | 0.251 | 0.507* | 0.4712** |
| DTT      | Before lockdown | −0.300 | 0.046  | −0.349 | 0.405  | 0.053  | 0.153 | 0.226 | 0.313 | 0.286  |
|          | During lockdown | 0.950*** | 0.855* | 0.795 | 0.501  | 0.858* | 0.903* | 0.921** | 0.744 | 0.486  |
|          | Total           | 0.140 | 0.295  | −0.017 | 0.394  | 0.293  | 0.394 | 0.407 | 0.435* | 0.313  |

**Fig. 4.** Time series of the DTT activities, abundances of CHO$^+$ and CHON$^-$ of OA samples and their linear correlation during lockdown period.
Nevertheless, few of them have clarified the specific chemical species that were dominant in the ROS production (Chen et al., 2019; Li et al., 2019c). Ma et al. (2018) have identified the individual species of water-soluble HULIS associated with the oxidative potential of PM$_{2.5}$. It should be noted that the results may be limited due to the small number of samples collected during the lockdown. In-depth research with an increased sample should be conducted in the future to further investigate the correlation between the atmospheric species and their oxidative potential during the lockdown period.

4. Conclusions

Different from previous studies that focused mainly on the macroscopic level of chemical species, this research investigated the specific molecular composition of OAs and the relation between these species and the OP of PM$_{2.5}$ before and during the COVID-19 lockdown period. The results showed a relatively higher reduction of atmospheric pollutants including PM$_{2.5}$, PM$_{10}$, SO$_2$, NO$_x$, and CO in Linfen, China compared to the national mean level during the lockdown period. Similar to other cities and regions, the level of O$_3$ in Linfen increased by 52.5% synchronously, which in turn enhanced the atmospheric oxidizing capacity. All the subgroups in OAs showed a decline in their abundance ranging from $-7.09\%$ to $-32.59\%$ during the lockdown period. Sulfur-containing CHOS and CHONS compounds showed the highest decreasing rate of 27.85%, indicating a vast reduction of fossil fuel combustion caused by the lockdown measures. Compared to the large decrease of oxygen amine CHON $+\text{ compounds}$ (27.57%), nitro (NO$_2$) or nitroxy (ONO$_2$) functional CHON-compounds have shown a relatively lower decrease rate of 7.09%, which may be associated with the weaker nitrate radical chemistry caused by the diminution of NO$_x$. As high-condensed azaarenes and aromatic amines take a vital position in the CHN compounds, a relative decrease of 23.95% may imply the decline in the health risk of PM$_{2.5}$. Change in the oxidative potential of OAs has verified the result as it has declined by 8.76% during the lockdown period. Besides that, a high correlation was observed between the abundance of CHO- ($r = 0.950$, $p < 0.001$) and the level of DTT activities during the lockdown, so was CHOS- ($r = 0.921$, $p < 0.001$). The likelihood that these components become the predominant contributor to the oxidative potential of PM$_{2.5}$ in the quarantine period is thus rather high. The overall correlation between secondary-formatted OOs and the concentration of PM$_{2.5}$ as well as that between nitroxy-OSs and PM$_{2.5}$ have shown to increase after the implementation of the lockdown measures, while the correlation between these organic species and the direct emitted PM$_{10}$ and CO has decreased, suggesting an enhanced secondary formation of OAs to the total concentration of PM$_{2.5}$ during the lockdown period. The above observations manifest the validity of the joint-control strategy during the COVID-19 lockdown period in controlling the anthropogenic emission thus reducing the level and health risks of numerous atmospheric pollutants. Enhanced secondary formation of OAs associated with the high atmospheric oxidation capacity should be taken into consideration in the future to further reduce the pollution level.

Credit author statement

Wei Wang: Writing original draft, Data curation, Formal analysis, Methodology. Yanhao Zhang: Data curation, Writing-review & editing, Methodology. Guodong Cao: Methodology, Resources. Yuanyuan Song: Resources. Jing Zhang: Resources. Ruijinn Li: Resources. Lifang Zhao: Resources. Chuan Dong: Resources. Zongwei Cai: Supervision, Manuscript editing and revising, Resources, Project administration.

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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