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Elevated particle acidity enhanced the sulfate formation during the COVID-19 pandemic in Zhengzhou, China

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ABSTRACT

The significant reduction in PM$_{2.5}$ mass concentration after the outbreak of COVID-19 provided a unique opportunity further to study the formation mechanism of secondary inorganic aerosols. Hourly data of chemical components in PM$_{2.5}$, gaseous pollutants, and meteorological data were obtained from January 1 to 23, 2020 (pre-lockdown) and January 24 to February 17, 2020 (COVID-lockdown) in Zhengzhou, China. Sulfate, nitrate, and ammonium were the main components of PM$_{2.5}$ during both the pre-lockdown and COVID-lockdown periods. Compared with the pre-lockdown period, even though the concentration and proportion of nitrate decreased, nitrate was the dominant component in PM$_{2.5}$ during the COVID-lockdown period. Moreover, nitrate production was enhanced by the elevated O$_3$ concentration, which was favorable for the homogeneous and hydrolysis nitrate formation despite the drastic decrease of NO$_2$. The proportion of sulfate during the COVID-lockdown period was higher than that before. Aqueous-phase reactions of H$_2$O$_2$ and transition metal (TMI) catalyzed oxidations were the major pathways for sulfate formation. During the COVID-lockdown period, TMI-catalyzed oxidation became the dominant pathway for aqueous-phase sulfate formation because the elevated acidity favored the dissolution of TMI. Therefore, the enhanced TMI-catalyzed oxidation affected by the elevated particle acidity dominated the sulfate formation, resulting in the slight increase of sulfate concentration during the COVID-lockdown period in Zhengzhou.

1. Introduction

Fine particulate matter with an aerodynamic diameter of less than 2.5 μm (PM$_{2.5}$) has significant effects on the ecological environment, global radiation balance, and human health (Huang et al., 2014; Othman et al., 2020). The intensive emission of pollutants has led to high concentrations of PM$_{2.5}$ in Northern China due to rapid economic development. Numerous studies in this region have confirmed that SNA (sulfate, nitrate, and ammonia) accounted for more than 50% of PM$_{2.5}$ and increased significantly during the haze episodes (Cao et al., 2012; Liu et al., 2016; Zhang et al., 2013; Zheng et al., 2015). Consequently, many strict emission controls have been taken by the Chinese government and succeeded in reducing primary pollutants. However, the inadequate control on SNA often resulted in high PM$_{2.5}$ concentrations (Song et al., 2019; Wang et al., 2019c). Thus, studying the formation mechanism of SNA is of great significance to the reduction of PM$_{2.5}$.

The oxidation of NO$_2$ dominates the formation of nitrate in the gas-phase and heterogeneous hydrolysis of N$_2$O$_5$ on the existing wet aerosol surface in Northern China (Ji et al., 2014; Wang et al., 2019a; Wang et al., 2020b). Fu et al. (2020) reported that abundant O$_3$ and OH radicals during haze events were beneficial to converting NO$_2$ to nitrate in winter. Wu et al. (2018) found that the increase of aerosol water content (AWC) promoted the transformation of reactive gaseous pollutants to particles and intensified formation haze formation in the North China Plain. Influenced by the decrease of intensity of solar radiation and the increase of relative humidity (RH), aqueous-phase reactions have been proven to be the dominant pathway for sulfate formation during haze episodes in Northern China (Wang et al., 2012). In general, aqueous-phase sulfate formation is achieved by absorption of SO$_2$ into pre-existing wet particles or cloud droplets, followed by oxidation associated with O$_3$, H$_2$O$_2$, and NO$_2$ or catalyzed by transition metal ions (TMI, e.g., Fe (III) and Mn (II)) (Li et al., 2011; Seinfeld and Pandis, 2016).
Aerosol acidity (pH) is an important factor for SNA formation through affecting the ionic state of S(IV), the dissolution rate of TMI, and the gas-particle partitioning of semi-volatile and volatile species (Chu et al., 2016; Guo et al., 2017; Seinfeld and Pandis, 2016; Wang et al., 2019a). For aqueous-phase sulfate formation, acidity is positively correlated with the oxidation rates of O2 and NO2, negatively correlated with TMI-catalyzed oxidation, and has a negligible effect on H2O2 (Liu et al., 2020; Shi et al., 2017; Wang et al., 2020b). The oxidation of NO2 and O3 dominated the sulfate formation under the moderately acidic condition (a particle pH range of 4.5–7.0) in Beijing (Guo et al., 2017; Liu et al., 2017a). H2O2 and TMI-catalyzed oxidation exhibited a great contribution to droplet-mode sulfate formation in Zhengzhou, with a particle pH range of 4.0–5.5 (Wang et al., 2020b). The particle acidity was determined by chemical composition and meteorological conditions. For example, acidity was mainly affected by sulfate, NH3, and AWC in Beijing (Liu et al., 2017a), ammonia was the dominant factor affecting pH in Zhengzhou. The sensitivity of temperature (T) to pH value was higher than that of RH (Wang et al., 2020b). At present, the policy of reducing SNA in China mainly relies on controlling its precursor emission.

During the Corona Virus Disease 2019 (COVID-19) outbreak at the end of 2019, the Chinese government quickly implemented a series of measures to reduce people’s gathering, including traffic control and factory closure. Under the conditions of extreme emission reduction, the concentration of NO2 dropped to an unprecedented low value in most areas of China (Huang et al., 2020; Xu et al., 2020; Zheng et al., 2020). The national mean change rate of NO2 was ~35.7% (Zheng et al., 2020). Huang et al. (2020) found that NO2 decreased by more than 60% in eastern China. The concentration of NO2 in Wuhan, the first city to take lockdown measures, decreased by 55.6% (Zheng et al., 2020). However, the concentrations of SO2 remained stable, and O3 further increased (Pei et al., 2020). Moreover, unexpected haze events occurred in North China Plain (Wang et al., 2020a). The enhanced formation of SNA may partly explain the puzzling haze events, despite the decreased concentration of gaseous precursors. For example, the observed concentration of SNA during the lockdown period was 60% higher than that of the same period last year in Shanghai (Chang et al., 2020). Observation and model studies suggest that the increased atmospheric oxidation capacity enhances the formation of secondary species and almost offset the primary emission reduction (Huang et al., 2020). So far, increasing research on this typical haze event has been reported. However, the differences in SNA formation pathways are still unclear, and there is a lack of detailed acidity analysis on sulfate formation after the outbreak of the COVID-19 pandemic.

In this study, hourly data, including chemical components of PM2.5, gaseous pollutants, and meteorological variables, were collected by a series of online monitoring instruments from January 1 to February 17, 2020. The particle pH value was estimated by using the ISORROPIA-II model. The main purposes of this study are as follows: (1) studying the changes of PM2.5 compositions and formation pathways of SNA before and after the outbreak of the COVID-19; and (2) exploring the differences in the formation pathways of aqueous-phase sulfate and investigating the effects of pH on sulfate formation. This work is helpful to understand the SNA formation mechanisms and provide guidance for the future development of emission control measures.

2. Experiment and methods
2.1. Sampling and analysis

The measurements were conducted from pre-lockdown (January 1 to 23, 2020) to COVID-lockdown (January 24 to February 27, 2020), on the roof of a six-story building (about 20 m above the ground) in Zhengzhou University (34°48' N; 113°31' E). Detailed information can be found in (Yang et al., 2020). The site is close to residential areas, surrounded by busy roads, and there is a coal-fired power plant 6 km to the southeast (Fig. S1 of Supplemental Materials).

The ambient ion monitor (URG-9000D, Thermal Science, USA) was used to continuously measure water-soluble inorganic ions (NO3-, SO42-, Cl-, Na+, NH4+, K+, Mg2+, and Ca2+) and trace gases (HNO3, HCl, NH3, and HONO). Organic carbon (OC) and elemental carbon (EC) were quantified by NIOSH (National Institute for Occupational Safety and Health) 5040 thermal-optical transmittance method using a semi-continuous carbon analyzer (Model-4, Sunset Laboratory, USA). Hourly concentrations of metallic elements in the PM2.5 samples, such as Fe and Mn are detected by an energy dispersive x-ray fluorescence instrument (Xact-625, Cooper environmental services, USA). The hourly concentrations of H2O2 were monitored by an automatic continuous H2O2 analyzer (AL2021, AERO LASER, Germany) based on the peroxi-dase reaction of gas and liquid samples. PM2.5 concentrations were measured by a particulate matter online instrument (TEOM 1405, Thermo Fisher Scientific, USA).

SO2, NO2, CO, and O3 concentrations were obtained by being of online analyzers (Model 42i, 43i, 48i, and 49i, Thermo Fisher Scientific, USA). Wind speed (WS), temperature (T), and RH were measured simultaneously by an automatic weather station (QZX1.0, Yigu Technology, China). The analysis related to the working principle of the sampling instrument, quality assurance/quality control, and measurement uncertainties can be found in the Supplement (Text S1) were presented in our previous studies (Wang et al., 2019b; Yang et al., 2020; Ye et al., 2018).

2.2. The ISORROPIA-II model

The ISORROPIA II model can simulate the thermodynamic equilibrium of K+, Ca2+, Mg2+, NH4+, Na+, SO42-, NO3-, Cl-, H2O2 aerosol system to calculate the pH value and AWC of aerosol particles under aerosol equilibrium state. Input to ISORROPIA-II included chemical components (K+, Ca2+, Mg2+, NH4+, Na+, SO42-, NO3-, Cl-, HCl, HNO3, HONO, and HNO3 + NO3−) and meteorological variables (i.e., T and RH). ISORROPIA-II can estimate the mass concentration (µg m−3) of hydrous ion (H+aq) and AWC, and then the pH value can be calculated by the following formula:

$$pH = -\log_{10} \frac{H^+}{aq} = -\log_{10} \frac{1000H^+}{AWC}$$  \hspace{1cm} (1)

There are stable and metastable conditions that can simulate the thermodynamic equilibrium of aerosols in the ISORROPIA-II model. Stable state refers to the precipitation of salt in the aerosol when it reaches saturation in the aqueous phase, while metastable refers to the salt always in the aqueous phase without considering its saturated pre-

tion (Fountoukis and Nenes, 2007). Considering the high RH level recorded in the sampling period, the aerosol system was operated in metastable conditions. There are two modes in the model. The forward-mode calculations using the total concentrations of gas and aerosol species as inputs are less affected by these measurement errors. The reverse-mode calculations using the only aerosol-phase composition as inputs are sensitive to the measurement errors. The sensitivity depends on whether anions or cations are in excess, leading to unreliable particle pH estimates. (Ding et al., 2019; Guo et al., 2017; Liu et al., 2017a). Therefore, forward-mode was used in this study.

3. Results and discussion
3.1. Overview of air pollutants

The anthropogenic emissions significantly changed after the COVID-lockdown in comparison with those during the pre-lockdown. Fig. 1 shows the difference in the time series of major chemical components of PM2.5, typical gaseous pollutants including NO2, SO2, O3, HONO, and NH3, and meteorological variables in Zhengzhou with average values listed in Table 1. Compared to the pre-lockdown period, the PM2.5...
concentrations during the COVID-lockdown period decreased with the average values from 116 ± 55 to 83 ± 54 μg m⁻³. The concentration of NO₂ was reduced by 60%, associated with the sharp reduction of vehicle emissions after the lockdown (Ji et al., 2020). In addition, the increased WS during the COVID-lockdown period was favorable for the decrease of PM₂.₅ and NO₂, because high wind speed promotes the dispersion of pollutants and consequently weakens the process of pollutant accumulation and decreases secondary transformation (Gao et al., 2015; Zheng et al., 2016). Conversely, the concentration of SO₂ slightly increased, which may be attributed to the stable emissions of coal and biomass combustions for heating and cooking during the COVID-lockdown period (Cui et al., 2020; Xu et al., 2020). Moreover, the concentration of O₃ increased three times during the COVID-lockdown period, which was similar to the observation in most Chinese cities (e.g., Chengdu, Shenyang, Wuhan, and Jinan) (Sharma et al., 2020; Sokhi et al., 2021). Model results in eastern China suggested that the significant decrease in NOₓ emissions led to a substantial increase in O₃ concentration because O₃ was sensitive to the VOC reduction after the COVID-19 lockdown (Chu et al., 2020). Additionally, Yu et al. (2021) reported that VOCs controlled O₃ formation in Zhengzhou. Therefore, the significant decrease of NOx during the COVID-lockdown period may lead to the increase in the O₃ concentration. On the other hand, particulate matter was negative correlation with light radiation (Fu and Chen, 2017). Thus, the low particulate concentration during the lockdown was low, conducive to the formation of O₃. In addition, the increase of temperature after the lockdown was also further conducive to the formation of O₃ (Dueñas et al., 2002).

3.2. Enhancement of secondary transformation

The observation period was divided into three pollution levels to investigate the variations of chemical composition in PM₂.₅: clean period (PM₂.₅ ≤ 75 μg m⁻³), pollution period (75 < PM₂.₅ ≤ 150 μg m⁻³), and heavy pollution period (PM₂.₅ > 150 μg m⁻³). As shown in Fig. 2, SNA was the dominant component of PM₂.₅ during both the pre-lockdown and COVID-lockdown periods, accounting for 58–69% and 55–63%, respectively. Moreover, the percentages of SNA in PM₂.₅ increased with the aggravation of pollution, especially the proportions of NO₃⁻ and SO₄²⁻, respectively increased from 25% to 13% during the clean period to 31% and 15% during the heavy pollution period during the COVID-lockdown. In addition, another major component, organic matter (OM) showed a downward trend (Fig. 2). Therefore, SNA formation played a crucial role in PM₂.₅ increase even during the COVID-lockdown period in Zhengzhou.

Compared with the pre-lockdown period, the concentration and proportion of nitrate to SNA during the COVID-lockdown period decreased by 33% and 6%, respectively, revealing the lockdown had a powerful effect on nitrate reductions. However, nitrate remained the largest composition in PM₂.₅ during the COVID-lockdown period. On the other hand, the disproportionate drop of nitrate compared to NO₂ concentration (60%) implied the improved conversion of NO₂ during the COVID-lockdown period. Furthermore, the nitrogen oxidation ratios (NOR = NO₃⁻/(NO₂⁻ + NO₃⁻)), representing the conversion rate of NO₂ during the COVID-lockdown period (0.08–0.72) were significantly higher than those during the pre-lockdown period (0.06–0.61) under all pollution levels (Fig. 3a). Therefore, nitrate formation was enhanced relative to NO₂ emission reduction during the COVID-lockdown period, which was consistent with the characteristics of Beijing and Shanghai (Chang et al., 2020; Huang et al., 2020). As for sulfate, the proportions of SO₄²⁻ were slightly increased, accompanied by elevated sulfur oxidation ratios (SOR = SO₄²⁻/(SO₂²⁻ + SO₄²⁻)) during the COVID-lockdown period (Fig. 3b), demonstrating the greater importance of sulfate formation during the COVID-lockdown periods in Zhengzhou.

3.3. Formation of nitrate

The homogeneous reaction of NO₂ with OH radicals and hydrolysis of N₂O₅ are the main routes for nitrate formation during haze episodes in this region (He et al., 2018; Liu et al., 2020; Wang et al., 2019b, 2020b). HNO₃ production is generated by NO₂ + OH gas-phase reaction during the day, making the initial nitrate rapidly accumulate. The heterogeneous hydrolysis of N₂O₅ under high humidity conditions dominates the production of HNO₃ at night. O₃ mainly affects nitrate formation by participating in the formation of OH radicals and oxidizing NO₂ to NO₃ radical (He et al., 2018). Therefore, nitrate formation has a strong dependence on O₃ concentration and RH (Cheng et al., 2015; He et al.,...
The relationships between nitrate and NOR as a function of O$_3$ and RH are illustrated in Fig. 4a and b with their diurnal variations presented in Fig. 4c and d. NOR showed an obvious upward trend with COVID-lockdown periods. O$_3$ and RH are illustrated in Fig. 4a and b with their diurnal variations during the COVID-lockdown period were significantly higher than those during the pre-lockdown period. However, the RH-dominated NOR values changed little. Diurnal variations (Fig. 4c and d) show that O$_3$ concentration significantly increased throughout the day. RH decreased in the daytime and slightly changed at night during the COVID-lockdown. Zhengzhou is mainly under the NH$_3$-rich condition in winter, therefore, nitrate formation is controlled by HNO$_3$ availability (Wang et al., 2020c). Fu et al. (2020), using the Community Multiscale Air Quality model in the North China Plain region reported that the formation of HNO$_3$ is mainly limited by the oxidants OH and O$_3$ produced by the photochemical reaction of NOx and VOC. In addition, compared to the pre-lockdown period, the concentration of HONO, another main precursor for OH radical, during the COVID-lockdown period decreased with the average values from 4.7 ± 3.9 to 3.0 ± 2.3 μg m$^{-3}$ (Table 1). A high concentration of O$_3$ supports the formation of HNO$_3$. Therefore, the elevated O$_3$ concentration was favorable for the homogeneous and hydrolysis nitrate formation despite the drastic decrease of NO$_2$ during the COVID-lockdown period, which was consistent with other COVID-19-related studies (Chang et al., 2020; Huang et al., 2020; Lv et al., 2020; Xu et al., 2020).

### 3.4. Formation of sulfate

Studies in Zhengzhou have reported that aqueous-phase reactions dominated the sulfate formation during haze episodes (Wang et al., 2020b; Yang et al., 2020). Similarly, high SOR values (above 0.4) were mainly dominated by RH during both the pre-lockdown and COVID-lockdown periods (Fig. 5a and b, respectively).

### Table 1

A summary of the values (Mean ± SD) of the major chemical components in PM$_{2.5}$, gaseous species, and meteorological variables under different levels of pollution.

|                      | Pre-lockdown |                      | COVID-lockdown |                      |
|----------------------|--------------|----------------------|----------------|----------------------|
|                      | C, PM$_{2.5}$ < 75 (105 h) | P, 75 ≤ PM$_{2.5}$ ≤ 150 (214 h) | HP, PM$_{2.5}$ > 150 (130 h) | Mean ± SD (449 h) | C, PM$_{2.5}$ < 75 (243 h) | P, 75 ≤ PM$_{2.5}$ ≤ 150 (234 h) | HP, PM$_{2.5}$ > 150 (28 h) | Mean ± SD (504 h) |
| PM$_{2.5}$ (μg m$^{-3}$) | 47 ± 15 | 107 ± 22 | 186 ± 23 | 116 ± 55 | 48 ± 20 | 100 ± 15 | 252 ± 79 | 83 ± 54 |
| SO$_2$ (μg m$^{-3}$) | 9.6 ± 2.6 | 10.3 ± 3.7 | 9.2 ± 3.2 | 9.9 ± 3.3 | 8.7 ± 3.0 | 11.5 ± 4.1 | 14.2 ± 5.0 | 10.3 ± 5.1 |
| NO$_2$ (μg m$^{-3}$) | 44.8 ± 17.4 | 58.6 ± 14.3 | 61.6 ± 13.0 | 56.3 ± 16.2 | 19.0 ± 9.0 | 25.4 ± 10.7 | 27.6 ± 7.0 | 22.4 ± 10.2 |
| CO (mg m$^{-3}$) | 0.8 ± 0.2 | 1.1 ± 0.3 | 1.7 ± 0.3 | 1.2 ± 0.4 | 0.7 ± 0.2 | 1.1 ± 0.2 | 2.4 ± 0.7 | 1.0 ± 0.5 |
| O$_3$ (μg m$^{-3}$) | 42.3 ± 24.4 | 26.6 ± 21.2 | 21.9 ± 20.8 | 28.9 ± 23.1 | 71.1 ± 28.0 | 73.6 ± 29.4 | 81.5 ± 20.1 | 73 ± 28 |
| EC (μg m$^{-3}$) | 2.0 ± 0.5 | 3.1 ± 1.3 | 4.3 ± 1.2 | 3.2 ± 1.4 | 1.6 ± 0.7 | 2.5 ± 0.6 | 4.7 ± 0.3 | 2.1 ± 0.9 |
| OM (μg m$^{-3}$) | 13.0 ± 2.7 | 18.4 ± 6.1 | 23.9 ± 5.2 | 18.5 ± 6.5 | 13.9 ± 5.7 | 19.7 ± 4.9 | 32.4 ± 1.9 | 17.1 ± 6.5 |
| SO$_4^{2-}$ (μg m$^{-3}$) | 4.5 ± 2.4 | 10.1 ± 5.5 | 17.7 ± 5.5 | 11.0 ± 6.9 | 6.3 ± 2.8 | 13.0 ± 2.8 | 27.4 ± 8.1 | 10.7 ± 6.3 |
| NO$_3$ (μg m$^{-3}$) | 15.6 ± 8.7 | 31.5 ± 9.8 | 47.2 ± 11.7 | 32.4 ± 15.2 | 12.4 ± 5.1 | 25.2 ± 5.4 | 66.5 ± 23.3 | 21.7 ± 15.1 |
| NH$_4$ (μg m$^{-3}$) | 8.2 ± 3.3 | 15.6 ± 4.4 | 23.2 ± 4.4 | 16.1 ± 6.8 | 8.5 ± 3.0 | 15.4 ± 2.3 | 32.7 ± 9.6 | 13.2 ± 6.9 |
| HONO (μg m$^{-3}$) | 5.3 ± 3.5 | 4.0 ± 3.4 | 5.6 ± 4.7 | 4.7 ± 3.9 | 2.6 ± 1.9 | 3.2 ± 2.5 | 5.1 ± 3.4 | 3.0 ± 2.3 |
| NH$_3$ (μg m$^{-3}$) | 16.1 ± 7.8 | 12.8 ± 6.2 | 15.6 ± 8.0 | 20.9 ± 10.7 | 12.5 ± 5.6 | 15.5 ± 8.2 | 25.6 ± 6.9 | 14.4 ± 7.3 |
| H$_2$O$_2$ (μg m$^{-3}$) | 1.0 ± 0.3 | 1.0 ± 0.3 | 1.0 ± 0.1 | 1.0 ± 0.3 | 0.7 ± 0.2 | 0.9 ± 0.1 | 1.0 ± 0.2 | 0.8 ± 0.2 |
| WS (m s$^{-1}$) | 1.6 ± 0.9 | 1.2 ± 0.7 | 1.2 ± 0.6 | 1.3 ± 0.7 | 1.5 ± 1.0 | 1.3 ± 0.8 | 2.5 ± 0.7 | 1.5 ± 0.9 |
| T (°C) | 4.5 ± 2.5 | 3.6 ± 2.4 | 3.8 ± 2.3 | 3.8 ± 2.3 | 8.6 ± 4.5 | 6.0 ± 2.7 | 5.3 ± 1.8 | 7.2 ± 3.9 |
| RH (%) | 50 ± 21 | 68 ± 16 | 77 ± 8 | 67 ± 18 | 57 ± 24 | 66 ± 13 | 72 ± 8 | 62 ± 20 |
The sulfate production rates of aqueous-phase reactions, such as $\text{S(IV)}$ oxidation by $\text{H}_2\text{O}_2$, $\text{O}_3$, TMI, and $\text{NO}_2$, were calculated to identify further the major factors on sulfate formation (Cheng et al., 2016; Seinfeld and Pandis, 2016). Detailed calculation methods can be found in the Supplemental Materials (Text S2). The parameters for determining sulfate production rate during the pre-lockdown and COVID-lockdown periods are listed in Table 2, with their diurnal variations presented in Fig. S2. Aerosol pH has an important effect on sulfate production based on the results of the ISORROPIA-II. To verify the validity of the ISORROPIA-II thermodynamic model in estimating pH, we compared observed and predicted chemical compositions and gas concentrations. As shown in Fig. S3, the observed and predicted $\text{NO}_3^-$, $\text{NH}_4^+$, $\text{Cl}^-$, and $\text{NH}_3$ exhibit significant correlations, with correlation coefficients ($r$) above 0.99 and slopes near 1. Affected by the measurement uncertainty caused by low gas concentration, the correlation between $\text{HNO}_3$ and $\text{HCl}$ was weak (Ding et al., 2019; Liu et al., 2017b; Weber et al., 2016). It is worth noting that the pH value decreased from 4.5 to 4.9 (pre-lockdown) to 4.0–4.4 (COVID-lockdown). As shown in Fig. S4, during the COVID-lockdown, the $\text{TNH}_x$ average concentration decreased from 1.76 to 1.57 $\mu\text{mol m}^{-3}$, reducing particle pH from 4.5 to 4.3 units. Changes in mean values of $\text{NO}_3$ and $\text{TH}_2\text{SO}_4$ have limited effects on predicted pH. The concentrations of $\text{TNa}$, $\text{TCl}$, and $\text{Ca}^{2+}$ decreased slightly, and these species can reduce the predicted pH by about 0.01 units. In addition, the low RH also leads to the increase of pH during the COVID-lockdown period. The temperature rises higher after the lockdown (from 276 to 284 K), reducing the predicted pH value from 4.5 to 4.2 units. Among the chemical components of PM$_{2.5}$, the decrease of aerosol pH was driven mainly by $\text{TNH}_x$. Under meteorological conditions, the decrease of pH value was most affected by temperature.

Particle acidity was positively correlated with the sulfate production rate through $\text{O}_3$ and $\text{NO}_2$ oxidation and negatively correlated with TMI-catalyzed oxidation by affecting the composition of S(IV), oxidation rate constant, and dissolution rate (Guo et al., 2017, 2018; Liu et al., 2020; Wang et al., 2020b, 2020c). The sensitivity test of the impact of pH on...
Fig. 4. The relationships between NOR and NO$_3^-$ and during the Pre-lockdown (a) and COVID-lockdown (b) periods. The circle size and color scale represent the concentration of O$_3$ and RH, respectively. The diurnal trends of NOR, RH, O$_3$, and NO$_3^-$ during the Pre-lockdown (c) and COVID-lockdown (d) periods. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

Fig. 5. The relationships between SOR and SO$_4^{2-}$ during the Pre-lockdown (a) and COVID-lockdown (b) periods. The circle size and color scale represent the concentration of O$_3$ and RH, respectively. The diurnal trends of SOR, RH, O$_3$, and SO$_4^{2-}$ during the Pre-lockdown (c) and COVID-lockdown (d) periods. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)
the sulfate production rates was performed as shown in Fig. 7. The effect of pH on H$_2$O$_2$ oxidation rate can be ignored. NO$_2$ and O$_3$ oxidation rates increase with increasing pH, as well as TMI-catalyzed oxidation decreasing with pH. The trend is consistent with the above research about pH sensitivity. Fig. 6 compares the difference in diurnal variations of the four aqueous-phase sulfate production rates between the pre-lockdown and COVID-lockdown periods. H$_2$O$_2$ and TMI-catalyzed oxidations were the dominant pathways for aqueous-phase sulfate formation during the pre-lockdown and COVID-lockdown periods, consistent with the reported results observed in Beijing and Zhengzhou (Liu et al., 2020; Wang et al., 2020). During the COVID-lockdown period, TMI-catalyzed oxidation for aqueous-phase sulfate formation increased by 3.5 times at 9:00 compared with that during the pre-COVID period, and the rates increased from 0.019 to 0.105 mg m$^{-2}$ h$^{-1}$. As shown in Fig. 5S, the significant decreases in the concentration of Fe and Mn during the COVID-lockdown period were observed, the dissolved Mn(II) concentration still decreased despite the acidity increase. Moreover, the concentration of Fe(III) increased slightly, but Fe(III) had a lower effect on sulfate formation (Fig. 5Sb). The elevated acidity facilitated the TMI-catalyzed oxidation rates after the COVID-lockdown (Fig. 5). On the contrary, the rate of H$_2$O$_2$ oxidation decreased during the COVID-lockdown period, which might be attributed to the lower concentration of H$_2$O$_2$ (Table 1). In addition, the elevated acidity resulted in low rates of O$_3$ oxidation because more S(IV) was in the state of SO$_2$-H$_2$O with a low oxidation rate constant (Xue et al., 2016). The NO$_2$ oxidation rate constant was negatively related to particle acidity (Wang et al., 2020), and thus the production rate of NO$_2$ oxidation decreased along with the less NO$_2$ concentration during the lockdown. In Fig. 7, during the COVID-lockdown period, the sum of the aqueous-phase sulfate production rates of four routes (TMI + NO$_2$ + O$_3$ + H$_2$O$_2$) is greater than before. As for the total aqueous-phase sulfate production rates during the COVID-lockdown period, the enhanced TMI-catalyzed oxidation reaction rates at daytime can offset the reduction of the other three oxidation pathways and hence lead to the high total aqueous-phase sulfate production rates increasing of 2–179% compared with those during the pre-lockdown period. Therefore, the enhanced TMI-catalyzed oxidation affected by the elevated particle acidity dominated the sulfate formation and resulted in the slight increase of sulfate concentration during the COVID-lockdown period in Zhengzhou. In addition, the elevated particle acidity was also beneficial to the gas-particle partitioning of NH$_3$ into NH$_4^+$ and prevented a significant decrease in the NH$_4^+$ concentration (Liu et al., 2017a; Wang et al., 2020b).

3.5. Uncertainties

To estimate the uncertainties of aqueous sulfate-producing rates by input data, an uncertainty analysis was conducted. Therefore, we made an uncertainty analysis. First, we estimated the pH uncertainty based on sensitivity tests of pH to input data (Fig. S4). Particle pH is positively correlated with the cation concentrations (i.e., TNH$_4$, TNa, K$^+$, Ca$^{2+}$, and Mg$^{2+}$) and negatively correlated with the anion concentrations (i.e., TH$_2$SO$_4$, TNO$_3$, and TCI), T, and RH. Moreover, the pH value has a positive correlation with OC concentrations. For the maximum pH, adjust the cation and OC concentrations to the maximum positive uncertainties, and negatively correlated with the anion concentrations (i.e., TNH$_4$, TNa, K$^+$, Ca$^{2+}$, and Mg$^{2+}$) and negatively correlated with the anion concentrations (i.e., TH$_2$SO$_4$, TNO$_3$, and TCI), T, and RH. Moreover, the pH value has a positive correlation with OC concentrations. For the maximum pH, adjust the cation and OC concentrations to the maximum positive uncertainty; Anions, RH, and T are adjusted within their maximum negative uncertainty. For the pH-min case, set the above factors to the opposite case. Sensitivity tests of AWC are illustrated in Fig. S7. Positive parameters (i.e., TNH$_4$, TNO$_3$, TH$_2$SO$_4$, TNa, TCI, Mg$^{2+}$, and RH) were adjusted up to within their maximum positive uncertainties, and negative parameters (i.e., Ca$^{2+}$, K$^+$, and T) were adjusted down within their maximum negative uncertainties, which represented the AWC$_{max}$ case; For the AWC$_{min}$ case, the above factors were set to the opposite case. pH$_{max}$ and AWC$_{max}$ cases lead to 4% and 35% (slope–1) errors, respectively, pH$_{min}$, and AWC$_{min}$ cases result in approximately 6% and 26% deviations, respectively in Fig. S8. The uncertainty of H$_2$O$_2$, SO$_2$, and O$_3$ is 10%. Fe and Mn uncertainties were set to be 20%. The details can be found in the Supplement (Text S1).

Based on the sensitivity of pH, AWC, Fe, Mn, H$_2$O$_2$, SO$_2$, and O$_3$, the maximum and minimum rate scenarios of daily variation of four sulfate production rates were shown in Fig. 7. The sensitivity tests of sulfate production rates by altering inputs of pH.
production paths are calculated and illustrated in Fig. S9. Detailed data can be found in Table S3. TMI-catalyzed oxidation exhibit uncertainties in the range of −74–613%. Considering calculation uncertainties, markedly enhanced TMI-catalyzed oxidation rates are observed during the COVID-lockdown period (Fig. S9). Therefore, the oxidation pathway of TMI rather than H₂O₂ was found to contribute greatly to atmospheric sulfate formation during the COVID-lockdown period (Fig. S9).

4. Conclusions

Even though the concentration of NO₂ and nitrate decreased, the contribution ratio of nitrate to PM₂.5 during the COVID-lockdown period was the largest. Moreover, the nitrate formation was enhanced due to the elevated O₃ concentration, which was favorable for the homogeneous and hydrolysis nitrate formation during the COVID-lockdown period.

Sulfate formation had greater importance on PM₂.5 as a result of the slight increase in the concentrations and proportions of SO₄²⁻ as well as SOR during the COVID-lockdown period. Aquous-phase reactions of H₂O₂ and TMI-catalyzed oxidations were the dominant pathways for aqueous-phase sulfate formation during both the pre-lockdown and COVID-lockdown periods. However, during the COVID-lockdown period, TMI-catalyzed oxidation became the dominant pathway for aqueous-phase sulfate formation because the elevated acidity under low (HNO₃ + NO₂⁻)/SO₄²⁻ ratio in PM₂.5 favored the dissolution of TMI. Furthermore, the increased TMI-catalyzed oxidation reaction rates at daytime can offset the reduction of the other three oxidation pathways. Therefore, the enhanced TMI-catalyzed oxidation affected by the elevated particle acidity dominated the sulfate formation and resulted in the slight increase of sulfate concentration during the COVID-lockdown period in Zhengzhou.

Credit author statement

Shengbo Wang: Conceptualization, Methodology, Software, Writing - Review & Editing. Jieru Yang: Data Curation, Writing - Original Draft. Ruqin Zhang: Project administration, Funding acquisition Supervision. Shasha Yin: Supervision.

Data availability statement

The associated data can be downloaded online https://doi.org/10.5281/zenodo.4743611.

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.envpol.2021.118716.
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