Effects of Early Pollution Control Measures on Secondary Species of PM$_{2.5}$ in Jiaozuo, China

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**ABSTRACT:** Various measures for reducing air pollution have been promulgated since 2013 in China. To investigate the synergistic results of emission control and meteorological environment, PM$_{2.5}$ samples collected from October 2013 to July 2016 and November 2018 to October 2019 in Jiaozuo city were analyzed for their compositions, secondary species (Ss) variations, and factors changing for Ss formation. The results showed that the concentrations of sulfate, nitrate, ammonium, and secondary organic aerosols (SOAs) generally decreased over the same seasonal period during these years. In addition, the concentrations and proportions of each Ss increased with the increase in the PM$_{2.5}$ level in these years, implying that although PM$_{2.5}$ levels have been reduced by various control policies, Ss formation would remain the major contributor to PM elevations. The enhanced effects of gas-phase reactions on intensification of sulfate, SOA, and PM were observed in 2018–2019, which was consistent with the elevation of nitrate and SOA at PM levels of >150 μg/m$^3$. Only sulfate in all PM levels sharply decreased after 2015, showing the fine effect of coal-related pollution control and the importance of collaborative control of NO$_x$, volatile organic compounds, and organic aerosol emissions with SO$_2$ emissions in the future.

**1. INTRODUCTION**

Outdoor fine particles have been of high concern in China since 2013 due to their heavy contamination status and the serious impacts on environmental quality, physical health, and climate changes. In the meantime, the government promulgated various measures to reduce pollution and improve the air quality, such as the “Clean Air Action Plan (2013–2017)”. Previous studies have found that the concentrations and compositions of particles are based on their sources, especially human activities. Thus, it is significant to understand the variations of PM$_{2.5}$ components during the implementation of policies to evaluate the improvement of air quality and the development of subsequent mitigation strategies.

An extensive literature indicating that secondary species (Ss), that is, secondary inorganic aerosol (SIA) of sulfates, nitrates, and ammonium and secondary organic aerosol (SOA), are the major chemical constituents in PM$_{2.5}$. The haze formation is usually accompanied by a Ss increase in particles such as the January 2013 winter haze, driven by sulfate enhancement caused by heterogeneous oxidation. Primary emissions, levels of PM gas precursors, meteorological conditions, regional transport, and the efficiency of secondary formation synergistically act on the formation of particles. Therefore, to demonstrate the synergistic results of source emission control and meteorological factors, the PM$_{2.5}$ composition variations and temporal patterns of Ss were analyzed based on the PM$_{2.5}$ samples collected from 2013 to 2016 and 2018 to 2019 in Jiaozuo.

Jiaozuo is located in the northwestern Henan province, one of the regions seriously polluted with particles in China. Its terrain inclines from the northwest to southeast, south of the Taihang mountains, which is the intersection of the south side and the east side of the Taihang Mountains, and is not conducive to pollution dispersion and the circulation of air with frequent stable meteorological conditions. Thermoelectricity and cement are major industries, and coal energy is the main energy consumed in Jiaozuo. It showed 16.96 million tons of raw coal consumption in 2016, increased by 11.5% compared to that in 2014, based on the statistical yearbook of Jiaozuo. However, the Jiaozuo government issued various measures to improve air quality from 2013 to 2016. The main contents, promulgation time, and the phased implementation effects of the clean air measures issued by Jiaozuo government are listed in Tables S1 and S2. According to the statistics of the Jiaozuo
Ecological Environment Bureau, the air quality has been improved in Jiaozuo, with the annual mean concentrations of PM$_{2.5}$ decreasing from 86 in 2015 to 66 μg/m$^3$ in 2017. In addition to local emissions, the particulate level at this site is also comprehensively affected by the north–south and east–west airflows, which can reflect the overall level of PM decline in the region. By analyzing the implementation of the pollution control policy and the process of PM quality improvement, more effective control measures can be provided for the future.

2. RESULTS

2.1. Concentrations of PM$_{2.5}$ and Its Species. The average concentration of PM$_{2.5}$ was 101.5 ± 49.8 μg/m$^3$ during the study period, with great variations from 28.0 to 272.7 μg/m$^3$, which exceeded the Chinese daily grade II guideline of 75 μg/m$^3$ on 54.8% of the selected days. As the predominant species of PM$_{2.5}$, sulfate (SO$_4^{2-}$), nitrate (NO$_3^-$), ammonium (NH$_4^+$), organic carbon (OC), elemental carbon (EC), and crustal elemental oxides (CEO) accounted for 17.9, 15.9, 10.5, 14.3, 5.1, and 6.1%, respectively. According to the PM$_{2.5}$ reconstruction in Figure S2b, SIAs, SOAs, primary organic aerosols (POAs), EC, and CEO accounted for 44.3, 14.0, 8.9, 5.1, and 6.1%, respectively. Ss contributed 58.3% to PM$_{2.5}$ on average concentration of PM$_{2.5}$ was 101.5 ± 49.8 μg/m$^3$ in 2017. In comparison with ammonium bisulfate. Thus, although there were significant descent of NO$_3^-$ and SO$_4^{2-}$ in synchronization. Ammonia can react with SO$_2$ and NO$_2$ in the atmosphere to form ammonium bisulfate, ammonium sulfate, and ammonium nitrate. The equivalent charge between SO$_4^{2-}$ and NH$_4^+$ is 28.5, 56.6, 54.8, and 34.0% for NH$_4^+$, 55.8, 55.7, 57.4, and 37.7% for SOA, respectively. The effective control and reduction of SO$_2$ (Figure S3b) may cause the sulfate in PM$_{2.5}$ to decrease significantly and the heterogeneous reactions against SO$_2$ and NO$_3^-$ in the atmosphere to reduce. Although the possession of civil vehicles increased from 299,042 in the end of 2013$^{28}$ to 555,911 in the end of 2018,$^{29}$ the strict implementation of traffic restrictions made no significant increase in NO$_3^-$ in Jiaozuo. Two reasons made the significant descent of NO$_3^-$ and SO$_4^{2-}$ in synchronisation. The concentrations of Ss generally decreased over the same seasonal period during these years. It showed a significant dropping trend in spring, summer, and autumn from 2014 to 2019 and in winter from 2015 to 2018, with a reduction of 48.8, 59.6, 44.9, and 44.8% for SO$_4^{2-}, NO_3^-, NH_4^+, SOA, POA, EC, CEO, and trace elements (TE)] during the sampling period. Relevant data for winter 2016 and winter 2017 are from ref27.

2.2. Temporal Variations of Ss. The seasonal concentrations of conventional pollutants (NO$_2$, SO$_2$, and O$_3$), PM$_{2.5}$, and its major species during the sampling period are shown in Figures 1, S3, and S4. The concentrations of PM$_{2.5}$ presented clearly seasonal and inter-annual variations. The highest seasonal mass concentrations of PM$_{2.5}$ appeared in winter, followed by autumn, spring, and summer. The average winter concentrations of PM$_{2.5}$ were 1.0–1.3, 1.4–3.0, and 1.5–2.7 times those of other seasons in 2013–2014 (autumn 2013 to summer 2014), 2015–2016 (autumn to summer), and 2018–2019 (winter to autumn), respectively. Meanwhile, it showed a decreasing trend for the seasonal concentrations of PM$_{2.5}$ in the same period. The PM$_{2.5}$ concentrations decreased by 27.9, 53.0, and 52.1% in spring, summer, and autumn from 2014 to 2019, respectively, and by 31.7% in winter from 2015 to 2018. For autumn, there was no decreasing trend of seasonal PM$_{2.5}$ concentrations due to the lack of data from 2016 to 2018. However, the mean concentrations in autumn were significantly lower in 2019 than that in 2015.

3. DISCUSSION

3.1. Comparisons of Control Effect with Other Cities. Compared with the same season in other years, high levels of...
the concentrations of PM\textsubscript{2.5} and its components in autumn and winter were all observed in 2015. It indicated that growth dominated the concentrations of PM\textsubscript{2.5} before 2015. After that, each seasonal mean concentration of PM\textsubscript{2.5} and Ss began to show a downward trend. On carrying out the control measures related to coal combustion and emissions, such as controlling total coal consumption, desulfurization upgrade of coal-fired boilers, and shutdown of small coal-fired boilers (Table S2), the concentrations of SO\textsubscript{2} in each season showed a downward trend from winter 2013 (Figure S3b). The annual variations of the seasonal concentrations of NO\textsubscript{2} and O\textsubscript{3} were different from that of SO\textsubscript{2}. The mean O\textsubscript{3} concentration of each season in the same period decreased first (from autumn 2013 to summer 2015) and then increased. Each seasonal concentration of NO\textsubscript{2} showed a slight decrease since 2015. Overall, the concentrations of SO\textsubscript{2} and PM\textsubscript{2.5} in an outdoor environment in Jiaozuo have been getting better with the implementation of various policies and regulations on air pollution control, while that of NO\textsubscript{2} and O\textsubscript{3} have not.

According to the Henan energy balance sheet (actual quantity),\textsuperscript{20-33} the residential consumption of coal in the Henan province increased by 19.2% from 2013 to 2015, and the residential consumption of raw coal accounted for 21.0% of the total final consumption in 2015. In particular, coal consumption in rural areas, which rarely have pollution control measures, accounts for more than 70.0% of residential consumption until the end of 2015. Previous studies have found that the particles emitted by household coal combustion are mainly carbonaceous.\textsuperscript{34} Therefore, there were still higher concentrations of SO\textsubscript{2} and POA in PM\textsubscript{2.5}. Furthermore, the volume of SO\textsubscript{2}, NO\textsubscript{x}, and soot emission from urban life all increased from 2013 to 2015.\textsuperscript{28,35} For Jiaozuo, less than 20% of the city residents realized centralized heating before 2014 (https://www.henan.gov.cn/2014/08-12/533515.html), and the policy of replacing residential coal with gas and electricity was also in its infancy until winter 2015 (Tables S1 and S2). Decentralized coal combustion remained widespread. Additionally, by the end of winter 2015, measures resulting in the reduction of NO\textsubscript{2} emissions, such as denitrification upgrading in power and cement industry and elimination of the yellow-label and old vehicles, were still in the process and had not been completed. While the number of civil vehicles sharply increased from the year of 2013\textsuperscript{28} to 2015\textsuperscript{35} (increase by 21.7%), the concentrations of NO\textsubscript{2} in autumn and wintertime increased by 28.0 and 23.9% from 2013 to 2015, respectively. These reasons caused high levels of Ss in PM\textsubscript{2.5} before 2016. Moreover, NO\textsubscript{2} can catalyze the transformation of SO\textsubscript{2} and promote the formation of sulfate, nitrite, and ammonium.\textsuperscript{14}

The stable meteorological conditions in winter could significantly intensify secondary formations of precursors. Distinct to the buildup of PM\textsubscript{2.5} components in winter 2015, a significant decrease has been observed since 2016. With further implementation of specific control measures involving vehicles and coal-related industries (Tables S1 and S2), the precursors and primary particles showed a remarkable decrease (Figures S3 and S4), which leads to the apparent decline of PM\textsubscript{2.5} and Ss since 2016.

Considering that the joint prevention and control measures were adopted in Beijing–Tianjin–Hebei and surrounding areas before 2017, the study selected provincial cities surrounding Jiaozuo, including Beijing, Tianjin, Shijiazhuang, Taiyuan, Jinan, and Zhengzhou, to compare the temporal variations of air pollutants (PM\textsubscript{2.5}, NO\textsubscript{2}, SO\textsubscript{2}, and O\textsubscript{3}) and the control results between Jiaozuo and these cities (Figure S6). The control measures implemented in these cities are similar to those in Jiaozuo, which differ only slightly in timing and the degree of target requirements. It showed a similar temporal variation on these pollutants in the whole region. Although the concentrations of PM\textsubscript{2.5} and SO\textsubscript{2} varied from city to city in each season, the inter-annual variation was similar among these cities in each season, showing a decreasing trend. Also, the decreasing trend of SO\textsubscript{2} was very significant in all cities. Except for Jinan, no obvious inter-annual variation of NO\textsubscript{2} concentration was observed, indicating that NO\textsubscript{2} emission reduction measures have not achieved significant results in other cities. With the implementation of the policy, the seasonal O\textsubscript{3} concentration in all cities showed an increasing trend.

The concentration changes of Ss in PM are not exactly the same in surrounding cities after control measure implementation, but the general decreasing trend is similar for sulfate, such as a decrease of sulfate concentrations by 42.4% from 2013 to 2017 in Handan,\textsuperscript{36} by 11.0% from winter 2013 to winter 2016 in Beijing,\textsuperscript{16} and by 41.6% from winter 2016 to winter 2017 in cities along the Taihang Mountains.\textsuperscript{27} The variation trends of nitrate, ammonium, and SOA in PM\textsubscript{2.5} were not consistent in each city, and they may increase in some cities.\textsuperscript{16,36} However, the concentrations of these three Ss decreased to different degrees in most surrounding cities,\textsuperscript{27} which was consistent with the variations in Jiaozuo.

3.2. Species Contributions at Different Particle Levels. The concentrations and proportions of major

![Figure 2](https://dx.doi.org/10.1021/acsomega.0c04169)
components at different PM$_{2.5}$ levels in Jiaozuo were reconstructed and analyzed (Figure 2). It was divided into four levels based on the PM$_{2.5}$ concentration: $<75$, 75−150, 150−250, and $>250$ μg/m$^3$. It can be clearly seen that the concentrations of all major species show an increasing trend with the increase in PM$_{2.5}$ concentration. SO$_4^{2−}$, NO$_3^{−}$, SOA, and NH$_4^+$ were the most obviously increasing components with the increase of PM$_{2.5}$ pollution level, followed by POA, EC, CEO, and TE. The concentrations of SIA were 21.6, 49.9, 95.2, and 131.4 μg/m$^3$ at the level of PM$_{2.5}$ $<75$, 75−150, 150−250, and $>250$ μg/m$^3$, which was 3.0, 3.2, 3.8, and 3.2 times that of SOA, respectively.

The trend of species proportion in PM$_{2.5}$, however, was not exactly consistent with its concentration variations as PM level increased. The proportion of POA, EC, CEO, and TE in PM$_{2.5}$ decreased with increasing pollution, while that of SO$_4^{2−}$, NO$_3^{−}$, and SOA increased. Although the proportion of NH$_4^+$ fluctuated, it was higher at the level of PM$_{2.5}$ $>150$ μg/m$^3$ than that at PM$_{2.5}$ $<150$ μg/m$^3$. The increment of SO$_4^{2−}$ proportion was in agreement with the enhanced sulfate formation during China’s severe winter haze episode in January 2013. The OC/EC was 2.5, 2.8, 3.5, and 4.3 from low to high PM levels, respectively [when OC/EC > 2, there could exist secondary organic carbon (SOC)38,39], which is consistent with the SOA reconstructions at different PM$_{2.5}$ levels (Figure 2). Overall, the mass fractions of primary species in PM$_{2.5}$ decreased from 25.1 to 12.6% when the PM$_{2.5}$ concentrations increased from $<75$ to $>250$ μg/m$^3$ level, while the fractions of Ss increased from 52.4 to 66.2%. Additionally, the proportions of SIA in PM$_{2.5}$ were 2.1, 2.6, 3.3, and 5.2 times that of SOA under the four levels, respectively. It could be ascertained that secondary matter was the major contributor to PM$_{2.5}$ elevations, and the secondary inorganic species dominated the atmospheric PM$_{2.5}$ in heavy polluted weather.

The variation trend of concentrations and proportions of each species with the increase of PM$_{2.5}$ levels were also applicable in 2013−2014, 2014−2015, 2015−2016, and 2018−2019 (Figure 3). The concentrations of PM$_{2.5}$ primary species, and Ss decreased gradually during 2013−2014 to 2018−2019 at PM$_{2.5}$ levels of $<75$ and 75−150 μg/m$^3$. However, these concentrations were first increased and then decreased for Ss and slowly increased for primary species at PM$_{2.5}$ $>150$ μg/m$^3$ level during 2013−2014 to 2018−2019. Meanwhile, the proportions of Ss decreased basically during 2013−2014 to 2018−2019 at each PM$_{2.5}$ level, although they were the highest in 2015−2016 at PM$_{2.5}$ $>150$ μg/m$^3$ level. The proportions of Ss were 53.3, 60.1, and 60.6%, from low to high PM$_{2.5}$ levels in 2013−2014, 51.2, 56.2, and 66.5% in 2015−2016, and 51.8, 49.5, and 58.5% in 2018−2019, respectively. There was a high proportion of Ss at each PM$_{2.5}$ level, especially at the high level, which indicated that the secondary formation was the major contributor to PM$_{2.5}$ elevations for a long time and would remain so.

Similarly, the concentrations and proportions of SO$_4^{2−}$, NO$_3^{−}$, NH$_4^+$, and SOA varied considerably at the same PM$_{2.5}$ levels. The OC/EC was higher at PM levels of 75−150 μg/m$^3$ than that at PM levels of 75−150 μg/m$^3$, which was 3.0, 3.2, 3.8, and 3.2 times that of SOA, respectively. Additionally, the average concentration of each Ss fluctuated slightly, their concentrations decreased year by year. At PM levels of 75−150 μg/m$^3$, the concentrations of SO$_4^{2−}$ decreased the most from 24.1 μg/m$^3$ in 2013−2014 to 14.0 μg/m$^3$ in 2018−2019, followed by Ss, NH$_4^+$, and NO$_3^{−}$. It was decreased by 3.5 μg/m$^3$ for SOA, 2.2 μg/m$^3$ for NH$_4^+$, and 1.6 μg/m$^3$ for NO$_3^{−}$. Obvious decreasing of sulfate concentrations in particles at the same PM level indicated the remarkable effect of controlling measures related to coal.

At PM levels of $>150$ μg/m$^3$, the concentrations of each Ss were the highest due to the high PM$_{2.5}$ concentrations in 2015−2016. Hence, their proportions were mainly compared during these years. Compared to that in 2013−2014, the proportions of SO$_4^{2−}$ in PM$_{2.5}$ sharply decreased by 8.3%, and its concentrations also decreased by 11.4 μg/m$^3$ in 2018−2019. NH$_4^+$ was slightly decreased by 0.8% in proportion (0.1 μg/m$^3$) from 2013−2014 to 2018−2019. The variations of SO$_4^{2−}$ and NH$_4^+$ were consistent with that at PM levels of 75−150 μg/m$^3$. However, Ss and NO$_3^{−}$ were observed to be increasing by 6.1% (11.4 μg/m$^3$) and by 0.7% (0.8 μg/m$^3$) from 2013−2014 to 2018−2019, respectively. Several reasons for this are as follows. First, the substantial reduction of atmospheric SO$_2$ caused a decrease of SO$_4^{2−}$ formation.

Figure 3. (a) Concentrations and (b) mass fractions of major species in 2013−2014, 2014−2015, 2015−2016, and 2018−2019 at different PM$_{2.5}$ levels. The data of winter 2014 (2014−2015) were missing.
Moreover, when the proportion of SO$_4^{2-}$ in PM$_{2.5}$ is lower than 20%, the inhibitory effect of sulfate on the formation of nitrate$^{37}$ may be weakened, which further promotes the formation of nitrate in turn. Second, there was still abundant NO$_2$ to form NO$_3^-$ in 2018−2019 compared with that in 2013−2014 (Figure S3d). The increase in the number of vehicles led to the increase in NO$_2$ emissions in recent years. The ratio of NO$_3^-$/SO$_4^{2-}$ is usually used to reflect the relative contribution of mobile and stationary sources to particles.$^{40,41}$ In this study, it was 0.8 and 0.6 in 2013−2014, 1.0 and 1.0 in 2015−2016, and 1.2 and 1.0 in 2018−2019 at PM levels of 75−150 and >150 μg/m$^3$, respectively. It suggested that the stationary sources were the major contributors to particles of higher concentrations at the early stage of sampling. While the NO$_3^-$/SO$_4^{2-}$ ratios generally increased in 2015−2016 and 2018−2019 at higher PM levels, indicating that the relative contributions of mobile sources to form PM$_{2.5}$ increased. Meanwhile, because of the cleaner national six standards for vehicles that have not been implemented before 2019, the increase of vehicles would inevitably lead to the increase of primary carbon components and organic gaseous precursor emissions. However, only at PM levels of >150 μg/m$^3$, the concentrations and proportions of SOA increased from 2013−2014 to 2018−2019. Also, PM concentrations more than 150 μg/m$^3$ were all observed in winter. Therefore, this accumulation of SOA was the result of the large volume of precursors produced by vehicle exhaust and coal burning and then superimposed with meteorological effects. It also indicated that precursors accelerate the formation of secondary organics in a statically stable environment. On the whole, in addition to controlling emissions from coal-fired sources, it is also necessary to collaboratively control the emission of vehicle exhausts to improve air quality.

### 3.3. Factors Changing Sulfate and Nitrate Formation.
Sulfate and nitrate can be either directly emitted from primary emissions,$^{11,25}$ or generated by gas-phase reactions, aqueous reactions in cloud or fog droplets, and heterogeneous processes associated with aerosols.$^{42}$ For example, Li et al. found 33% of sulfate was from primary emissions in winter 2014 in Xi’an.$^{25}$ Sulfur oxidation ratio (SOR) and nitrogen oxidation ratio (NOR) are usually used to characterize the oxidized degree of SO$_2$ and NO$_x$, respectively, and to identify the formation processes of sulfate and nitrate. SOR is the molar ratio of [SO$_4^{2-}$] to [SO$_4^{2-}$+SO$_2$], and NOR is the molar ratio of [NO$_3^-$] to [NO$_3^-$+NO$_2$]. Sulfate mainly comes from primary emissions when the SOR < 0.1, while it mainly comes from secondary transformations when the SOR > 0.1.$^{43}$ The larger the SOR value is, the greater the photochemical reaction takes place, and the more obvious secondary transformations are. Similar to the SOR, the larger the NOR value is, the more obvious NO$_x$ conversions are.

From PM$_{2.5}$ levels of <75 to >150 μg/m$^3$, the SOR values were 0.15, 0.20, and 0.22 in 2013−2014, 0.14, 0.21, and 0.27 in 2015−2016, and 0.39, 0.35, and 0.40 in 2018−2019, respectively. The NOR values were 0.12, 0.24, and 0.25 in 2013−2014, 0.11, 0.17, and 0.31 in 2015−2016, and 0.13, 0.22, and 0.27 in 2018−2019 from low to high PM levels, respectively. It can be seen that the sulfate and nitrate in PM$_{2.5}$ at each PM level in those years was mainly derived from the secondary particles produced by the photochemical reaction or aqueous/heterogeneous processes. Except for SOR in 2018−2019, the value of SOR and NOR at high PM levels were both higher than those at low levels in those years, indicating the higher oxidation rate of SO$_2$ and NO$_x$ at high PM levels. The chemical process producing sulfate and nitrate was based on meteorological conditions and reaction medium.
There are several pathways for the oxidation of SO\textsubscript{2} and NO\textsubscript{2}\textsuperscript{42} to sulfate and nitrate, respectively. The dissolution of NO\textsubscript{2} and SO\textsubscript{2} can be oxidized into sulfate via the oxidation by OH radical in the gas phase, and by ozone, hydrogen peroxide, organic peroxy radicals, oxygen, and nitrogen dioxide in bulk aqueous phase or under high relative humidity (RH) conditions. Homogeneous gas-phase oxidation of NO\textsubscript{2} by OH and O\textsubscript{3} and the heterogeneous reactions of NO\textsubscript{2} with O\textsubscript{3} are the two important pathways for nitrate formation. To reveal the changes of factors affecting the formation of sulfate and nitrate, SOR and NOR were paired with T, RH, and O\textsubscript{3} concentrations in Figures 4 and S7.

SOR and NOR showed weak correlation with temperature (T) (Figure S7), indicating that temperature had little influence on SOR and NOR\textsubscript{13} similar results were also found in Handan by Zhao et al.\textsuperscript{36} and in Beijing by Zhang et al.\textsuperscript{13} Moreover, there were no obvious correlations between SOR and O\textsubscript{3} and it only showed an observable trend of decrease at RH > 60% to 0.33 ± 0.09 and 0.16 ± 0.09 at RH < 60% to 0.33 ± 0.04 and 0.37 ± 0.08 at RH > 60% in 2013–2014, from 0.16 ± 0.09 and 0.14 ± 0.09 at RH < 60% to 0.23 ± 0.09 and 0.23 ± 0.10 at RH > 60% in 2015–2016, and from 0.34 ± 0.09 and 0.16 ± 0.06 at RH < 60% to 0.44 ± 0.09 and 0.17 ± 0.06 at RH > 60% in 2018–2019, respectively. This result suggested that the increases of RH could promote the formation of nitrate and sulfate. The dissolution of NO\textsubscript{3} and SO\textsubscript{2} enhances with increasing RH, which is the foundation of the subsequent transformation in the aqueous/heterogeneous phase oxidation process. Previous studies\textsuperscript{44,45} found that low RH (usually <40\%) favors homogeneous gas-phase reactions, and high RH favors heterogeneous gas–particle reactions. It is worth noting that O\textsubscript{3} concentration tended to decrease with the increase of RH (Figure S8). The environment of strong solar radiation and low RH favors photochemistry and suppresses heterogeneous reactions. As the RH increases and the O\textsubscript{3} concentration decreases, the formation of sulfate and nitrate from heterogeneous processes gradually increases. It suggested that aqueous/heterogeneous chemical processes played an important role in the formation of SO\textsubscript{4}\textsuperscript{2−} and NO\textsubscript{3}−.

The results of the reaction process are also absolutely affected by the content of gas precursors. The influence of the atmospheric precursors on the chemical constituents in PM\textsubscript{2.5} is notable,\textsuperscript{14,46} especially the increase of SO\textsubscript{2} which can not only increase SO\textsubscript{4}\textsuperscript{2−} in the particulate matter, but also promote the NO\textsubscript{3}− content to some extent. For example, because of the low concentrated gas supply rate and large-scale retail coal cooking and winter heating, the concentration of SO\textsubscript{2} in Jiaozuo was significantly higher than that in Beijing (Figure S10). NO\textsubscript{3}− in PM\textsubscript{2.5} in Jiaozuo was slightly higher than that in Beijing (+3.1 μg/m\textsuperscript{3}) in winter 2016–2017,\textsuperscript{16} even with the lower NO\textsubscript{2} (7.6 μg/m\textsuperscript{3} in Jiaozuo and 81.7 μg/m\textsuperscript{3} in Beijing). The ratio of (NO\textsubscript{3}− /NO\textsubscript{2})\textsubscript{Jiaozuo}/ (NO\textsubscript{3}− /NO\textsubscript{2})\textsubscript{Beijing} was 1.2, showing that NO\textsubscript{3}− was more easily formed in Jiaozuo due to the high SO\textsubscript{2} concentration. Moreover, SOR and NOR were close before summer 2016 in Jiaozuo, with the values of 0.20 and 0.21 in 2013–2014 and 0.18 and 0.17 in 2015–2016. Additionally, there were comparable concentrations of SO\textsubscript{2} and NO\textsubscript{2} before summer 2016. With the different decreasing rates of SO\textsubscript{2} and NO\textsubscript{2}, SOR increased to 0.37 and NOR decreased to 0.17 in 2018–2019, indicating that to some extent, the increase of the volume-mixing ratio of NO\textsubscript{2} in the atmosphere could effectively promote the gas to particle conversion of SO\textsubscript{2}. It was consistent with the conclusion drawn in previous studies that a high concentration of NO\textsubscript{2} promotes sulfate formation by heterogeneous and aqueous oxidation of SO\textsubscript{2}.

According to the conceptual model proposed by Li et al.,\textsuperscript{24} the relative contributions were reduced for photochemical reactions and increased for heterogeneous processes with the increase in RH. In the process, it simultaneously showed ozone decrease, the positive feedback of particles and enhanced SIA formation. It was mentioned that SOR and NOR increased with the elevation of PM level in the previous section. O\textsubscript{3} concentrations were found to be decreasing with the increase of particle (Figure S9) and SIA concentrations in 2018–2019. RH corresponding to the initial significant increase of sulfate (~40–80%) was observed to be decreasing with the increase of volume-mixing ratio of NO\textsubscript{2} and NH\textsubscript{3} by Wang et al.\textsuperscript{14} However, no matter at high or low RH level, SOR was greatly elevated and was higher than NOR in 2018–2019 compared with other years, whereas NOR showed a small change. Furthermore, the concentrations of sulfate and nitrate merely increased by 3.50 and 2.12 from 16.28 and 12.16 μg/m\textsuperscript{3} at RH <60% to 19.78 and 14.28 μg/m\textsuperscript{3} at RH >60% in 2018–2019, respectively, and the increments were markedly smaller than that in other years. Therefore, the efficient formation of sulfate in 2018–2019 may depend not only on the relative enhancement of heterogeneous reactions but also partly on the intensification of the gas-phase oxidation of SO\textsubscript{2}.

3.4. Incremental Contributions of Organic Matter to Particles. The OC/EC ratio can be used to characterize the emission sources and the conversion characteristics of carbon aerosols, depending on both the proximity of the emissions and the relative weight of road traffic and biomass burning. The daily OC/EC ratios were in the range of 1.4–4.2 with an average of 2.5, 2.4, and 3.5 in 2013–2014, 1.3–4.8 with an average of 2.3, 2.7, and 3.6 in 2015–2016, 1.3–5.6 with an average of 2.8, 3.5, and 4.8 in 2018–2019 for PM levels ranging from low to high, respectively. Previous studies have found that the OC/EC ratio of road traffic emissions varies between 1.4 and 5 for gasoline catalyst vehicles,\textsuperscript{53–55} from 0.3 to 1 for diesel vehicles,\textsuperscript{49,51–54} from 2.5 to 10.5 for coal smoke,\textsuperscript{55} from 4.3 to 7.7 for kitchen emissions,\textsuperscript{56} and larger values (3–70) for biomass burning emissions.\textsuperscript{75–76} It indicated that despite the difference in the OC/EC ratio between these years, the carbon components in these years were still mainly derived from fossil fuel combustion and vehicle emission.

SOC/EC can represent the chemical reaction rate, which is similar to OC/EC. The highest seasonal SOC/EC ratio generally appeared in wintertime and the lowest in summertime, which indicates the favorable conditions of winter to form SOC and was in agreement with the seasonal change of OC proportion. The seasonal variations of EC, primary organic carbon (POC), and SOC were shown in Figures 1 and S11. The concentration of carbonaceous species in autumn (19.7 μg/m\textsuperscript{3}) and winter (26.4 μg/m\textsuperscript{3}) was obviously higher than that in spring (19.3 μg/m\textsuperscript{3}) and summer (12.7 μg/m\textsuperscript{3}), the same as that of SOC. A large number of small coal-fired boilers and dispersed domestic coal burning still existed before 2018. It led to increased emissions of volatile or semi-volatile organic compounds (VOCs) and organic gases. The special climatic conditions in winter, such as low temperature and low mixing layers, are not conducive to the diffusion of carbonaceous gas and pollutants, allowing
them to remain in the atmosphere for long periods and to fully produce photochemical reactions. Therefore, it resulted in the content of SOC in winter increasing significantly, reaching 1.5 times that in autumn and 2.9 times that in summer.

The SOC/EC ratio increased with PM levels in each year, and it also increased year by year at the same PM level. It changed from 1.5, 1.5, and 2.0 in 2013−2014 to 1.7, 2.0, and 2.8 in 2018−2019 at the low to high PM levels in order, indicating that SOA was easily formed under severe pollution, and the favorable conditions to enhance SOA formation was continuously intensified. It is commonly believed that SOA can be formed by gas−particle partitioning of organic matter (OM) and heterogeneous reactions of oxygenated organics.42 Gas-phase reactions are dominated by absorptive partition of low-volatility and semi-volatile oxidation products associated with VOC emissions.42 Particle-phase reactions mainly include hydration reactions, acid-catalyzed reactions, and reactions with basic species.42 The meteorological conditions under different SOC/EC in these years were compared in Figures 4 and S7. SOC/EC did not correlate well with RH and temperature in these years, indicating that the changes of temperature and RH may have little difference on the formation of SOA. However, there was a relatively increasing trend and decreasing trend for SOC/EC with the increase of RH and temperature, respectively. It showed that increasing temperature promoted the volatilization of SOA from the particle phase to gas phase, and the hydroscopic property of particles also plays a role in the formation of SOA. The ratio of SOC/EC showed a decreasing trend at O₃ < 60 μg/m³ and an increasing trend at O₃ > 60 μg/m³ with the increase of O₃ concentrations. There was no obvious difference between these years, while O₃ in 2019 showed an increasing trend compared with other years. Low temperature, high O₃ concentrations, and high RH tended to enhance secondary OM in 2018−2019, that is, gas phase reactions seemed to be dominant in formation of SOA after 2018.

4. CONCLUSIONS

Various measures have been taken in many areas of China to prevent and control haze since 2013. To evaluate the initial effects on air quality after measure implementation, the variations of outdoor PM_{2.5} and its components from October 2013 to July 2016 and from November 2018 to October 2019 in Jiaozuo city were analyzed. The concentrations of PM_{2.5}, Ss generally decreased over the same seasonal period during these years. The total proportions of Ss decreased during 2013−2014 to 2018−2019 at each PM_{2.5} level, but there were still high proportions and increases with the increase of PM levels, indicating that the secondary formation was the major contributor to PM_{2.5} elevations. Moreover, due to similar measures, the inter-annual variations of seasonal concentrations of PM_{2.5}, SO_{2}, NO_{2}, and O₃ in Jiaozuo were consistent with that in surrounding cities, showing a decreasing trend for PM_{2.5} and SO_{2}, an increasing trend for O₃, and fluctuations for NO_{2}.

Sulfate and ammonium in the three PM levels have decreased by different degrees after 2015, but nitrate and SOA have increased significantly at high PM levels of >150 μg/m³. Nitrate and SOA were observed as having an increasing effect on particle enhancement, showing that the collaborative emission controls of NOₓ, VOCs, and organic aerosols should be strengthened in Jiaozuo. The enhanced effects of gas-phase reactions on the intensification of sulfate, SOA, and PM were also observed in 2018−2019, which was consistent with the elevation of nitrate and SOA. In addition, the significant decrease of sulfate after 2015 was mainly attributed to the sharp reduction of SO_{2}, indicating that compared with other pollution control measures, coal-related control measures played an important role in reducing PM_{2.5} first.

5. METHODS

5.1. Sample Collection. The sampling site was located on the rooftop of the school of resources and environment of Henan Polytechnic University in Jiaozuo, Henan province (Figure 5). The inlet was approximately 15 m above ground.
level, 1.5 km northeast of the high-tech district government site, a state-controlled air quality monitoring station. There were no obvious obstructions and pollution sources within 5 km of and around the sampling site. So, we assume that the composition of particles at this site represents the general situation of particulate matter in general in Jiaozuo. Sample collection and weighing process strictly referred to “technical specifications for gravimetric measurement methods for PM_{2.5} in ambient air” (HJ 656-2013). The 24 h integrated PM_{2.5} samples (8:00–7:30, UTC+8) were collected by prebaked (450 °C, 4 h) quartz membranes (MK 360, Munktell, Sweden, 8 × 10 in.) with a TFIA-2 high-volume air sampler (Staplex, USA) at flow rates of 1.05 m³/min. A total of 289 valid samples of PM_{2.5} in different seasons were monitored from October 2013 to July 2016 and from the end of November 2018 to mid-October 2019. The hourly average concentrations of PM_{10}, NO₂, SO₂, CO, and O₃ were based on the data from the high-tech district government site (http://222.143.24.250:100/flex/index.html). In addition, the hourly meteorological parameters such as temperature (T), WS, wind direction, RH, precipitation, and pressure were also recorded concurrently.

5.2. Composition Determination. The concentrations of main species in selected PM_{2.5} samples, that is, major inorganic elements, TEs, water soluble inorganic ions (WSII), OC, and EC were carried out. Inorganic elements, including Na, Mg, Al, Si, S, Cl, K, Ca, and Fe, were determined by X-ray fluorescence spectrometry (ARL Quant’X EDXRF, Thermo Scientific Inc., USA). The minimum detection limits (MDL) were within the range of 0.13–0.85 μg/cm² for these elements. Mercury (Hg) was measured by direct mercury analyzer from Milestone (DMA-80, Milestone, Italy). The instrument’s detection limit was 0.001 ng. Other TEs of Ni, Br, Cr, As, Ba, Co, Cu, Pb, Sb, Se, V, Zn, Mn, and Cd were analyzed by inductively coupled plasma/mass spectrometry (820-MS, Varian, USA), according to the determination of metals in ambient particulate matter (HJ 657-2013). The MDLs were within the range of 0.02–8 μg/L for these TEs. Samples were digested before the test. The digestion process of PM_{2.5} on the filters using microwaves was also performed according to HJ 657-2013. Water-soluble cations and anions were measured, including Ca²⁺, Mg²⁺, K⁺, Na⁺, NH₄⁺, SO₄²⁻, NO₃⁻, Cl⁻, and F⁻. The detailed operation for measuring WSII is as follows. Part of the sample was cut and placed in 10 mL of ultra-pure deionized water (>18.2 MΩ) for ultrasonic extraction for 30 min. Then, the extract was filtered through a lure syringe filter (0.45 μm). The ions were determined by ion chromatography (ICS-3000, Dionex Co., USA) after the filtration solution was fixed to 15 mL. MDLs were within the range of 1–11 μg/L for these WSII. OC and EC were measured by an OC/EC analyzer (DRI model 2001A, Atmoslytic Inc., USA), with the thermal reflection method (TOR, IMPROVE A protocol). The MDLs were 0.01 μg/cm² for EC and 0.39 μg/cm² for OC.

Field blanks and parallel samples were tested for composition determination. Field blanks were collected every tenth sample. Parallel experiments (n = 3 set for each parallel test) were conducted with reagent blanks, filter blanks, and 10% of the test samples. The reagent blanks and filter blanks were determined to ensure the blank value did not interfere with the determination of samples. Analytical precision was calculated as the relative standard deviation (RSD) from duplicates. The measured results showed that the RSD results were less than 15% for all parallel tests. The RSD ranged within 0.7–4.8% for major element analysis by EDXRF, 0.3–3.3% for mercury analysis by DMA, 0.9–12.6% for TEs analysis by MS, and 0.5–1.3% for carbon analysis.

5.3. Mass Reconstruction. In order to assess the chemical composition in PM_{2.5} thoroughly, reconstructed mass (RM-PM_{2.5}) was conducted on the basis of different PM_{2.5} pollution levels by considering SIA, SOA, POA, EC, CEO, and remaining TE.

SIA is the sum of SO₄²⁻, NO₃⁻, and NH₄⁺. OM was estimated as 1.6 times OC, which is based on the OM/OC ratios of 1.6 ± 0.2 for urban aerosols⁶⁹ and 1.6 ± 0.18 in PM_{2.5} for Northern Chinese cities⁶⁸ obtained in previous investigations. Furthermore, OC can be divided into POA and COA according to its sources and formation pathway. So, POA and SOA were estimated through the following formula: POA = 1.6 × POA = 1.6 × EC_{meas} × (OC/EC)_{min} and SOA = 1.6 × SOC = 1.6 × (OC_{meas} − POA). POA can be estimated using the minimum OC/EC ratio⁶⁸,⁶⁹,⁷⁰ because (OC/EC)_{min} is almost equivalent to the ratio of the local primary source affecting the measured concentrations when assuming only combustion sources of OC. CEO was calculated by the IMPROVE “soil” formula⁷¹ applying a factor of 1.16 for one oxide multipliers to account for unmeasured compounds, that is, CEO = 2.20 × Al + 2.49 × Si + 1.63 × Ca + 2.42 × Fe + 1.94 × Ti (assuming oxides of Al₂O₃, SiO₂, CaO, Fe₂O₃, FeO (in equal amounts), K₂O (assuming that soil K is 0.6 × Fe), and TiO₂). TEs were calculated as a sum of remaining elements (excluding S and geological elements).⁶⁸–⁷⁰ Because TEs only account for a small fraction of PM_{2.5} mass, variations in the assumptions regarding metal oxides or multipliers did not contribute to large variations in RM-PM_{2.5}. As a consequence, potential molecular forms were ignored for the remaining elements.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.0c04169.

Daily and seasonal changes of temperature, RH, concentrations of gas pollutants (CO, NO₂, SO₂, and O₃), and concentrations and mass fractions of PM_{2.5} species of selected samples; main contents, promulgation times and the phased implementation effects of the clean air measures issued by the Jiaozuo government during 2013–2016 (PDF).

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The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes
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