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Special Section: Atmospheric PM2.5 in China: physics, chemistry, measurements, and modeling

Key Points:
- Four pollutants (PM$_{2.5}$, SO$_2$, CO, and NO$_2$) declined and O$_3$ concentrations increased in the nine cities from 2016 to 2018.
- PM$_{2.5}$ was positively correlated with SO$_2$, CO, and NO$_2$, while O$_3$ had negative correlations with the other four pollutants.
- Clustering analysis shows the air pollution in the cities is mainly related to their industrial structures besides geographical location.

Supporting Information:
- Supporting Information S1
- Table S1
- Figure S1
- Figure S2
- Figure S3

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**Abstract**

Air quality in Northern China has become a global hot spot issue due to a series of air pollution events in the recent years. In this study, five representative air pollutants (PM$_{2.5}$, SO$_2$, NO$_2$, CO, and O$_3$) were employed to reveal the spatial and temporal distribution of air pollution in Northern China. Periodic decline in PM$_{2.5}$, SO$_2$, CO, and NO$_2$ from 2016 to 2018 indicated that air pollution control measures have achieved desired results. In addition, PM$_{2.5}$ was significantly positively correlated with SO$_2$, CO, and NO$_2$ ($p < 0.001$), and O$_3$ had negative correlations with the other four pollutants. Furthermore, the heavy pollution phenomenon in Shijiazhuang, Anyang, Xingtai, and Handan was attributed to their industrial structures (e.g., steel industry) and geographical location based on clustering analysis. Contrary to above four pollutants, the annual average concentrations of O$_3$ increased in all the nine cities (1.4–35.9%) from 2016 to 2018. It is necessary to plan mitigation strategy for O$_3$ based on further investigation of source and formation mechanism of O$_3$.

**Plain Language Summary**

Air pollution in Northern China has attracted many attentions due to continuous air pollution issues in the recent years. However, few studies focused on air pollution in the Beijing-Tianjin-Hebei transmission corridor. In this study, the spatiotemporal variation of air pollutants in nine typical cities was investigated. Pearson correlation analysis and clustering analysis were employed to analyze their relationship and reveal the pollution characteristic and the factors affecting the air pollution. This study provided an insight for the prevention and control of air pollution in Northern China.

1. **Introduction**

The Northern China is one of the most densely populated regions in the world and has suffered from severe atmospheric haze over the last two decades (Lu et al., 2019; S. Wang, Song, et al., 2019). Air pollution in China was previously estimated to contribute to 1.2 to 2 million deaths annually, approximately 17% of all deaths in China (Y. Li et al., 2016; Rohde & Muller, 2015; Streets et al., 2009; J.Zhang, Liu, et al., 2017). The extreme concentrations of representative air pollutants were captured in the corridor south of Beijing, that is, the Beijing-Tianjin-Hebei transmission corridor (Jie et al., 2018; X. Liu et al., 2010; Rohde & Muller, 2015). To mitigate air pollution in this area, the Chinese government implemented “Law on the Prevention and Control of Atmospheric Pollution” in 2015. In addition, “2+26” cities were selected with critical strategies in 2017 (H. Li et al., 2018), which were designed to manage the primary-fuel quality, combustion technology, and emission index for residents and industries (Tan et al., 2016; W. Wang et al., 2017). There is no time to delay to assess the risks arising by air pollution and to improve the air quality for human health. Hence, it is therefore essential to investigate the spatiotemporal variation of air pollutants among “2+26” cities in the recent 3 years.

A widespread air pollution episode occurred in Northern China in 5 January 2016 (Chen et al., 2017; Lang et al., 2017). Based on the data from the Ministry of Ecology and Environment of China, Anyang was listed in the top 10 worst pollution cities with the long duration of air pollution (Chen et al., 2017; Lang et al., 2017) in...
China, far worse than Beijing (S. Liu, Hua, et al., 2017; Rohde & Muller, 2015; Shen et al., 2017). It has been verified that industrial structure of the city is one of the important factors for local air pollution. Anyang is not only a typical heavy industrial city dominated by steelmaking and chemical industry but also is located on the Beijing-Tianjin-Hebei transmission corridor of air pollution. Pollutants immigration also has potential contribution for local air pollution. Besides Anyang, Zhengzhou, Hebi, Handan, Xingtai, and Shijiazhuang are also located on the transmission corridor and belong to the “2+26” cities of prevention and control for air pollution in China (Rohde & Muller, 2015). These cities mainly depended on iron and steel industry (Handan and Xingtai), petrochemical industry (Puyang), and coal industry (Hebi), and these industries usually yield different air pollution problems, whereas, Hangzhou, located in the Yangtze River delta industrial zone in Eastern China, is an electronic industrial metropolis and out of transmission corridor in Northern China. Therefore, Hangzhou can be selected as a reference city to compare with those cities on the transmission corridor in Northern China. The study on variation of air pollution in these cities will be beneficial to understand the characteristic of the Beijing-Tianjin-Hebei transmission corridor of air pollution (Bi et al., 2007; Rohde & Muller, 2015).

Previous research reported that PM$_{2.5}$ (particles with aerodynamic equivalent diameters ≤2.5 μm in the ambient air) was a primary pollutant of haze (Goodkind et al., 2019; K. Liu, Shang, et al., 2017). The components in PM$_{2.5}$ might pose a significant carcinogenic health risk to both children and adults (Y. Li et al., 2016; X. Li, Ju, & Kan, 2019; J. Zhang, Liu, et al., 2017). Dramatic increase trends of PM2.5 in China continued until 2007 (He et al., 2018; Ma et al., 2015; Van Donkelaar et al., 2014). Besides, ozone pollution has been an increasingly prominent in China and the national yearly concentrations of ozone in 2015 were higher than that in 2013 (W. Wang et al., 2017). Until now many studies revealed that PM$_{2.5}$ concentration had a close relationship with multiple geographic and socioeconomic factors (F. Huang et al., 2015; Lin et al., 2014). In addition, the associations between PM$_{2.5}$ concentration and meteorological factors had also been investigated (Yang et al., 2017; H. Zhang, Wang, et al., 2017). However, few studies focused on the spatial and temporal distribution of air pollution in the Beijing-Tianjin-Hebei transmission corridor and the relationship among different pollutants, including PM$_{2.5}$, SO$_2$, NO$_2$, CO, and O$_3$ (Editors, 2019; W. Wang et al., 2017; Westervelt et al., 2019). Additionally, it remains unclear which cities have similar pollution characteristic.

In this study, spatiotemporal variations of five air pollutants in the cities along the Beijing-Tianjin-Hebei corridor (Figure 1) were investigated based on monthly average concentrations. In order to reflect impact of adjacent areas, Hangzhou is selected as a reference city to compare with those cities on the transmission corridor in Northern China. The monthly and annual average concentrations of the five air pollutants were compared to the reference city Hangzhou. In addition, Pearson analysis was employed to reveal the relationship among these pollutants. Clustering analysis was employed to group the air quality of the nine cities and to describe the similarity based on their pollution characteristic. The objectives of this study are (i) to reveal the temporal and spatial variation of air pollution after the critical strategies were carried out in 2016, (ii) to identify the major pollutants, and (iii) to estimate the potential sources. This study provided an insight for the prevention and control of air pollution in the very recent years in Northern China.

### 2. Materials and Methods

The monthly data of five air pollutants, including PM$_{2.5}$, SO$_2$, NO$_2$, CO, and O$_3$ from 2016 to 2018, were obtained from the Data center of the Ministry of Ecology and Environment of China (China, 2019; J. Wang, 2019) (Table S1 in the supporting information).

The annual average concentrations of the five pollutants were calculated based on their monthly average concentrations using arithmetic average method by the following Equation 1. The results were listed in Table S1 in the supporting information. The decline rates of annual average concentrations of the five pollutants were obtained using equation 2.

\[
C_{\text{annual average concentration}} = \frac{\sum_{i=1}^{12} C_{\text{monthly average concentration}}}{12}
\]

\[
x\% \text{ (rate of decline)} = \left( \frac{C_{2016} - C_{2018}}{C_{2016}} \right) \times 100\%
\]
where \( x \% \) denotes the rate of decline in 2018 compared to 2016. A positive rate of decline indicates the concentration is declining and a negative rate indicates the concentration is increasing.

The Pearson’s correlation coefficients (\( r \)) were calculated between the monthly average concentrations (variables) of all the five pollutants for each of the nine cities over the three years (2016–2018). Pearson correlation analysis was performed using OriginPro 8.0 software (OriginLab Corporation). Differences were considered statistically significant at \( p < 0.05 \) (Hu et al., 2019; B. Liu, Wu, et al., 2017; Perrone et al., 2010; M. Song, Liu, Zhang, et al., 2019; Y. Wang et al., 2014).

A cluster analysis is a multivariate statistical technique that is widely used in air pollution research (Ali et al., 2016; Moura et al., 2019; M. Song, Liu, Zhang, et al., 2019). K-means cluster technique and Hierarchical cluster analysis are widely used cluster method (C. Song, Liu, Dai, et al., 2019). In this study, Hierarchical cluster analysis was applied to classify nine cities into different groups based on their monthly averages of the five pollutants in each city. The monthly concentrations in the hierarchical cluster analysis are variables. The aims are to examine relationships between the variables. The SPSS software (IBM SPSS20) for windows were used for the statistical analysis.

3. Results and Discussion

3.1. Variation of Monthly Average Concentrations

The variation of monthly average concentrations of the five air pollutants in the nine cities from January 2016 to February 2019 was shown in Figure 2. All the five pollutants varied significantly with seasons and exhibited a periodic cycle in a year.

The variations of PM\(_{2.5}\), SO\(_2\), CO, and NO\(_2\) are similar and significantly different to O\(_3\). The concentrations of PM\(_{2.5}\), SO\(_2\), CO, and NO\(_2\) were higher in winter (from November to February) as compared to summer (from May to August). For example, the highest monthly concentration of PM\(_{2.5}\) (276 \( \mu \)g/m\(^3\)) occurred in Shijiazhuang in December 2016, followed by Handan and Anyang (213 and 215 \( \mu \)g/m\(^3\),

![Figure 1. Scheme of the nine cities in the Beijing-Tianjin-Hebei transmission corridor of air pollution. The reference city Hangzhou is shown in the national wide map.](image)
respectively). The lowest monthly average concentration of PM$_{2.5}$ occurred in August in Hangzhou (25.2 μg/m$^3$) in 2016. The highest value of SO$_2$ occurred in January 2016 in Xingtai (107 μg/m$^3$), followed by Anyang in January 2016 (104 μg/m$^3$). The minimum of SO$_2$ in a year usually appeared in summer (2 μg/m$^3$ in August in Beijing). The highest monthly average concentration of CO was 4.03 mg/m$^3$ in January 2016 in Anyang, and the lowest monthly average concentration was 0.603 mg/m$^3$ in September 2018 in Beijing.

This trend varied with seasons of PM$_{2.5}$, SO$_2$, CO, and NO$_2$ (higher in winter and lower in summer) is related to the increased use of fossil fuels for heating and the frequent use of cars in winter (Xie et al., 2015). Moreover, the trend is also influenced by adverse meteorological conditions in winter, including temperature reverse, weak surface wind (O’Dell et al., 2019; Shu et al., 2017). Temperature inversion phenomenon readily occurs during winter, in the transmission corridor in Northern China (J. L. Wang et al., 2010). Adverse atmospheric diffusion conditions lead to accumulation of pollutants and aggravation of pollution (O’Dell et al., 2019; Shu et al., 2017; J. L. Wang et al., 2010).

The variation of monthly average concentrations of O$_3$ (Figure 2e) was opposite to PM$_{2.5}$, SO$_2$, NO$_2$, and CO, presenting a trend of higher in summer and lower in winter. The monthly average concentration of O$_3$ in summer was about 9 times higher than that in winter. The variations of O$_3$ implied a different formation mechanism of O$_3$ pollution from the other four pollutants (R.-J. Huang et al., 2014; W. Wang et al., 2017).

Figure 2. (a–e) Monthly average concentrations of the five air pollutants in the nine cities from 2016 to early 2019.

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To investigate the variation of air pollutants in summer and winter between 2016 and 2018, we calculated the decline rates in winter and summer (Figure 3 and Tables S2 and S3). For example, the average of PM$_{2.5}$, SO$_2$, CO, and NO$_2$ in winter 2018 fell by 17.5\text{–}55.1\% compared to 2016 winter. The decline in winter are higher than that in summer (10.0\text{–}29.8\%). On the contrary, the average O$_3$ of the nine cities in winter increased by 11.2\%, which is significantly (p < 0.05) less than that in summer (22.3\%). The decline in winter in Northern China benefits from the implementation of various air pollution control policies in the 3 years, such as shutdown of manufactures and vehicle restrictions during periods of heavy pollution (Liang et al., 2016). In addition, Li et al. reported that SO$_2$ emissions in China were reduced by more than 70\% since 2007, while NO$_x$ emissions in China remained high and decreased by 21\% from 2011 to 2015 (H. Li et al., 2018). We also observed that the decrease of SO$_2$ was higher than NO$_2$ from 2016 to 2018 (Figures 2b and 2d). Although the effects of the implementation policies for air pollution have been shown significantly, the adaptation and management should not be slack due to the absolute concentrations of pollutants are still higher in winter.

Moreover, there is little change between winter and summer in Beijing and Hangzhou for all the five pollutants. In order to characterize the extreme change in a year, we calculated the ratio of the highest to the lowest monthly concentration of SO$_2$ in 2016 and found that the ratio in Anyang city is as high as 9.5, while Hangzhou city is only 2.1 (less than others). Generally, the higher ratio reflected the more intense SO$_2$ emission in winter, which was associated with the energy structure of the city. In detail, people rarely use coal heating in Hangzhou, rather than power generation enterprise (Xie et al., 2015; Zheng et al., 2018). Therefore, the concentration of SO$_2$ and CO keeps steady between winter and summer in Hangzhou (Figure 2b). As a petrochemical city, the major fuel in Puyang is natural gas, and thus, SO$_2$ pollution in Puyang is significantly less than that of Anyang and Handan (p < 0.05), indicating SO$_2$ pollution in winter is linked to coal combustion for domestic heating. Additionally, Beijing is the capital of China and removed most of heavy industrial factories. While as typical heavy industrial cities, it is impossible for SJZ, Xingtai, Handan, and Anyang to remove their industrial factories. Actually, the above four industrial cities implement the critical ultralow emission standards since 2017 in coal fire power plants, steel, and coking factories (Wu et al., 2019), which led to significant decline of the concentrations of SO$_2$. However, the SO$_2$ emission is inevitable and the ratio of the highest to the lowest monthly concentration are still higher than Beijing, indicating the implementation of policies among different cities, as well as industrial conformation, energy structure and meteorological conditions, affect the concentrations of pollutants (Ma et al., 2015; Zhao & Luo, 2018).

### 3.2. Variation of Annual Average Concentrations

The annual average concentrations of the five air pollutants in the nine cities are shown in Figure 4. Generally, the annual averages of PM 2.5, SO$_2$, CO, and NO$_2$ decreased in most cities, which is contrary to O$_3$. Most annual averages of PM 2.5 and NO$_2$ exceed air quality standards of China during 2016–2018 (GB3095-2012).

The ranking order of PM$_{2.5}$ annual averages can be listed as follows based on the values in 2018: Shijiazhuang > Anyang > Handan > Xingtai > Puyang > Zhengzhou > Hebi > Beijing > Hangzhou (Figure 4a). Annual average concentration of PM$_{2.5}$ in Shijiazhuang in 2018 is 70.9 \mu g/m$^3$, followed by Anyang 70.0 \mu g/m$^3$. The PM$_{2.5}$ values varied greatly in different cities, which suggested that PM$_{2.5}$ pollution was influenced by the some factors, for example, different industrial structure, geographical location, and...
meteorological condition (Sun et al., 2016; Williams et al., 2012). Anyang, Xingtai, Handan, and Shijiazhuang mainly depended on iron and steel, chemical, and pharmaceutical industries, and their residential heating in winter mainly depends on coal combustion, which usually cause heavy internal pollution. Furthermore, these inland cities locate in the pollution transmission corridor among Beijing-Tianjin-Hebei; thus, PM$_{2.5}$ is difficult to diffuse due to adverse meteorological conditions. On the contrary, Hangzhou is an electronics industrial city and located in Eastern China. The pollution diffusion condition in this coastal city is better than those inland cities. Consequently, the pollution in the eight inland cities is much heavier than that in Hangzhou (p < 0.05 for all the five pollutants). It is well known that PM$_{2.5}$ is a complex pollutant. It is therefore necessary to further analyze other pollutants, such as SO$_2$, NO$_2$, CO, and O$_3$, with aims to reveal the source of pollution.

In 2018, SO$_2$ contamination in nine cities was ranked as follows: Xingtai > Anyang ≈ Shijiazhuang > Handan > Hebi > Puyang > Zhengzhou > Hangzhou > Beijing (Figure 4b). Only Beijing and Hangzhou meet the Grade I SO$_2$ standards GB3095-2012 (20 μg/m$^3$). Based on annual average concentrations in 2018, CO pollution in the nine cities can be ranked as follows: Anyang > Hebi > Xingtai > Handan > Shijiazhuang > Puyang > Zhengzhou > Hangzhou > Beijing (Figure 4c). The concentrations in Anyang (1.63 mg/m$^3$ in 2018) are nearly twice as high as that in Hangzhou (p < 0.05 for all the five pollutants). It is well known that PM$_{2.5}$ is a complex pollutant. It is therefore necessary to further analyze other pollutants, such as SO$_2$, NO$_2$, CO, and O$_3$, with aims to reveal the source of pollution.

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lower than the other cities ($p < 0.05$), which should be linked to the prohibition of coal burning except power plants (Finkelman & Tian, 2018; Y. Zhang, Liu, et al., 2018; Y. Zhang, Ye, et al., 2018; Zhao & Luo, 2018). This suggests that SO$_2$ and CO pollution in Beijing was mainly caused by urban biomass burning or coal burning.

Based on annual average concentrations of NO$_2$ in 2018, the NO$_2$ pollution can be ranked as follows: Zhengzhou > Xingtai > Shijiazhuang > Hebi > Anyang > Handan > Hangzhou > Beijing > Puyang (Figure 4d). The highest concentration is 50.3 $\mu$g/m$^3$ in Zhengzhou, and the lowest is 35.8 $\mu$g/m$^3$ in Puyang. NO$_2$ in the air mainly comes from vehicle exhaust gas, thermal power station, and other industrial fuel combustion, nitrogen fertilizer, and explosives (Huo et al., 2014). The variations of NO$_2$ with months are similar for all the nine cities (Figure 2d), but the decline of peak NO$_2$ concentration in winter over the 3 years is less than PM$_{2.5}$, SO$_2$, and CO (Figure 2). Moreover, the fluctuations of NO$_2$ in Beijing and Hangzhou are greater than SO$_2$ (Figure 2). These phenomena imply that major sources of NO$_2$ are inconsistent with PM$_{2.5}$, SO$_2$, and CO. There are a huge number of vehicles in Beijing (5.64 million vehicles in 2017), Hangzhou, and Zhengzhou (2.79 and 3.04 million vehicles in 2017, Table S4). In addition, the frequency of vehicle utilization, especially diesel trucks, significantly increases in winter, which might be one of reasons for the increase of NO$_2$ pollution in winter (H. Liu, Man, et al., 2017). It should be noted that some other factors, such as gas combustion, industry sources, and sources distribution in different cities, are also main reasons for NO$_2$ pollution (Guo et al., 2017).

In 2018, annual average concentrations of O$_3$ in the nine cities ranged as follows: Puyang > Handan > Hebi > Xingtai > Anyang > Shijiazhuang > Zhengzhou > Beijing > Hangzhou (Figure 4e). The highest annual concentration in 2018 is 117 $\mu$g/m$^3$ in Puyang, and the lowest concentration is 97.2 $\mu$g/m$^3$ in Hangzhou. The difference among the nine cities is not obviously significant ($p > 0.05$ for O$_3$ between Hangzhou, Beijing, and other seven cities, while $p < 0.05$ for PM$_{2.5}$, SO$_2$, CO, and NO$_2$ between Hangzhou, Beijing, and other seven cities). Unlike the other four pollutants, the little difference of O$_3$ pollution in the nine cities (Figure 2e) further validated that the main formation mechanism of O$_3$ could be similar, although the specific precursors (such as different volatile organic compounds, VOCs) and radical reactions might be different among these cities (R.-J. Huang et al., 2014; W. Wang et al., 2017).

To quantitatively compare the variation of five pollutants from 2016 to 2018, we calculated the rates of decline for annual average concentrations in 2018 compared to that in 2016 and listed them in Table 1.

Table 1

|                   | Beijing | SJZ | Xingtai | Handan | Anyang | Puyang | Hebi | ZZ | Hangzhou |
|-------------------|---------|-----|---------|--------|--------|--------|------|----|----------|
| PM$_{2.5}$        | 32.2    | 27.9| 21.6    | 14.5   | 18.5   | 12.2   | 29.9 | 26.5| 19.4     |
| SO$_2$            | 39.3    | 45.0| 50.5    | 47.4   | 56.7   | 43.4   | 55.1 | 47.6| 21.1     |
| CO                | 27.4    | 24.0| 20.2    | 30.4   | 28.3   | 21.1   | 28.6 | 28.7| −8.0     |
| NO$_2$            | 15.3    | 13.7| 18.7    | 22.1   | 12.8   | 14.2   | 14.6 | 9.2 | 6.3      |
| O$_3$             | −4.6    | −31.4| −35.9   | −29.6  | −31.6  | −13.8  | −22.3| −9.0| −1.4     |

Annual average concentrations of PM$_{2.5}$, SO$_2$ in the nine cities decreased significantly from 2016 to 2018 ($p < 0.05$, Table 1). The decline rates of PM$_{2.5}$ and SO$_2$ are from 12.2% (Puyang) to 32.2% (Beijing) and from 21.1% (Hangzhou) to 56.7% (Xingtai), respectively. The significant decrease shows that current pollution control measures are effective for PM$_{2.5}$ and SO$_2$ pollution. Annual average concentrations of CO decreased by 20.2% (Xingtai) to 30.2% (Handan) from 2016 to 2018, except Hangzhou (−8.0%, a negative rate implies the concentration are increasing). Annual average concentrations of NO$_2$ in the cities decreased by 6.3% (Hangzhou) to 22.1% (Handan), less than PM$_{2.5}$ and SO$_2$.

In addition, it should be noted that from 2016 to 2018, the annual concentrations of O$_3$ increased by 0.7% (Hangzhou) to 41.9% (Xingtai) in the nine cities. This trend is opposite to all the other pollutants, just like their monthly variations. To further identify the trends of O$_3$, we compared the O$_3$ concentrations before and after 2016 (Figure S1 and S2 and Table S5). We observed that, annual averages of O$_3$ concentrations from 2016 to 2018 increased by 1.4–35.9%, which are even higher than that from 2014 to 2015 for most cities,
except Hebi and Zhengzhou. This indicates that the major sources of the O$_3$ and the other pollutants are different and current pollution control strategies have little impact on O$_3$. O$_3$ is a secondary pollutant and results from photochemical reactions when primary pollutants, such as VOCs and NO$_2$, are exposed to...
sunlight (Xiao et al., 2018; Xie et al., 2015). The Chinese government released the Atmospheric Pollution Prevention and Control Action Plan in 2013, in which a series of measures have been adopted successively in this area (W. Wang et al., 2017). However, some important prosomal gases, such as VOCs, were not monitored because these gases do not constitute of the national air quality daily monitoring system (Zheng et al., 2018). The increasing O$_3$ pollution suggests that O$_3$ has become a major pollutant in Chinese cities. Thus, a combined pollution of PM$_{2.5}$ in winter and ozone in summer is becoming a major problem in China. It is therefore necessary to further reveal the mechanism of O$_3$ pollution and take effective measures to control O$_3$ pollution, especially in summer.

3.3. Correlation Analysis and Clustering Analysis

Pearson analysis was employed to quantitatively investigate the correlation of these pollutants using their monthly mean concentrations in the nine cities (Figure 5). Strong positive correlation between PM$_{2.5}$ with SO$_2$, CO, and NO$_2$ was observed (Figures 5a–5f) indicates that PM$_{2.5}$ pollution is mainly related to the emission and combustion of carbon, sulfur and nitrogen compounds (Xie et al., 2015). In addition, the significant correlation ($r = 0.8273$) between CO and SO$_2$ implies that the CO emission process might be accompanied by the emission of SO$_2$ (Figure 5e). Although NO$_2$ concentrations also correlated with PM$_{2.5}$, SO$_2$, and CO, its decline trend of winter peak over the 3 years is smaller than PM$_{2.5}$, SO$_2$, and CO (Figure 2), indicating NO$_2$ is not the main contribution for PM$_{2.5}$ and might be derived from different sources with SO$_2$. Interestingly, negative correlations between O$_3$ and the other four pollutants (Figures 5g–5j) were found in the nine cities over 3 years. Xiao et al. also found that areas with higher NO$_2$ concentrations tend to have lower O$_3$ concentration in southeast China (Z. Liu et al., 2015; Xiao et al., 2018; Xie et al., 2015). This might because O$_3$ is a secondary pollutant and could be generated by the photochemical reaction between NOx and VOCs (An et al., 2019; M. Wang, Yim, et al., 2019). In this process, high temperature is a key factor, and thus, NO$_2$ readily reacts in summer and difficult to react in winter due to low temperature. Maji et al. reported that an increasing VOCs level might be a main reason of the elevated O$_3$ (Maji et al., 2019). Previous studies reported that vehicles were the predominant contribution to ambient VOC concentrations (H. Liu, Man, et al., 2017; C. Song, Liu, Dai, et al., 2019). And ozone formation was caused by VOCs limited in urban areas and NOx limited in rural areas (Guo et al., 2017; C. Song, Liu, Dai, et al., 2019; X. Zhang, Xue, et al., 2017). Zheng et al. (2018) found that the total VOCs are increasing in China, and the mainly contributions are vehicle emissions, solvent use, and industry emission. In addition, decreases in PM$_{2.5}$ could stimulate the formation of ozone through changes both in aerosol chemistry and photoysis rates (Ding et al., 2013; K. Li, Jacob, et al., 2019). The main factor for ozone increase in the nine cities might be due to aerosol chemistry; namely, the decreased PM$_{2.5}$ slows down the reactive uptake of HO$_2$ radicals and leads to the increase of ozone (K. Li, Jacob, et al., 2019). Due to complicated formation mechanism, current pollution control measures have limited impact (or incompatible) on O$_3$ pollution (Chang et al., 2018; K. Li, Jacob, et al., 2019). We should further improve current prevention measures for O$_3$ control and decrease the emission of precursors of photochemical smog, for example VOCs (Ding et al., 2013).

The results of the clustering analysis based on the five air pollutants are shown in Figure 6. The nine cities could be classified into four groups. The first group is Hangzhou and showed a better air quality, and their PM$_{2.5}$ and CO and SO$_2$ were significantly lower than others ($p < 0.05$). This might be related to its geographic, meteorological factors and lower emissions of pollutants. Beijing is the second group. Although Beijing is located in Northern China and its geographic and socioeconomic factors are similar as other cities in the same area, its air quality is still better than these cities in the same area. This is because the city is the capital of China, and there are few heavy industrial manufactories in the city. The third group includes Zhengzhou, Hebi, and Puyang, with higher average concentrations than that in the first group ($p < 0.05$). In the fourth group, Anyang, Xingtai, Handan, and Shijiazhuang showed the closest distance, indicating the highest similitude among the four cities. We further calculated the averages of the four groups based on their monthly concentrations of five pollutants. The results indicate that Groups 3 and 4 are obviously
higher than Groups 1 and 2 for PM$_{2.5}$, SO$_2$, and CO (Figure S3). The clustering analysis indicates that air pollution is mainly related to their industrial structures besides geographic and socioeconomic factors. The four cities in the fourth cluster mainly depend on steel and chemical industry. Hebi and Puyang are not clustered into the same group with Anyang due to their different industrial structure, even though their distances from Anyang are far closer than Xingtai.

### 4. Conclusion

Monthly and yearly variations of PM$_{2.5}$, SO$_2$, NO$_2$, CO, and O$_3$ in nine typical cities from 2016 to 2018 were investigated. PM$_{2.5}$ and NO$_2$ were the two main pollutants, which exceeded the national quality standards (GB 3095-2012) in most cities. Four pollutants, including PM$_{2.5}$, SO$_2$, NO$_2$, and CO, showed a decreasing trend, while annual concentration of O$_3$ was continuously increasing from 2016 to 2018. The higher concentrations of PM$_{2.5}$, SO$_2$, NO$_2$, and CO in winter indicated that these pollutants were related to the increase of coal and biomass burning in winter. However, higher concentration of O$_3$ was observed in summer, which suggested that high temperature could be a dominated factor for O$_3$ formation besides precursors of O$_3$, such as VOCs and NO$_2$.

According to Pearson correlation analysis, PM$_{2.5}$ was positively correlated with SO$_2$, CO, and NO$_2$, indicating that PM$_{2.5}$ pollution was mainly related to combustion of carbon, sulfur, and nitrogen compounds. It is interesting that O$_3$ had negative correlations with the other pollutants, and formation of O$_3$ was mainly related to high temperature in summer. Based on cluster analysis, Anyang, Xingtai, and Hantan were grouped due to their air pollution is mainly related to their industrial structures (steel industry). On the contrary, Beijing and Hangzhou were grouped with the better air quality because they had developed tertiary industry.

Current measures of pollution control, such as shutdown of manufactures and pho-oxidative capacity limit, have significant effect on PM$_{2.5}$, SO$_2$, and CO and NO$_2$ pollution except O$_3$. Consequently, it is necessary to further investigate the source and formation mechanism of O$_3$, especially to develop new measures to control O$_3$ pollution in summer.

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