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Letter

Air Pollutant Correlations in China: Secondary Air Pollutant Responses to NO_x and SO_2 Control

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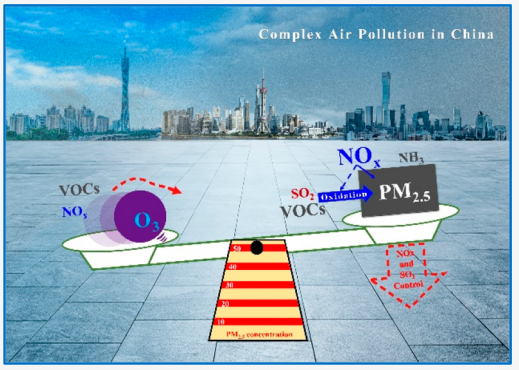
ABSTRACT: $PM_{2.5}$ concentrations have decreased remarkably in China in recent years, coinciding with a more rapid decrease in SO_2 concentrations and a slower decrease in NO_2 concentrations, while O_3 concentrations increased. Correlations between $PM_{2.5}$ and key gaseous pollutants were studied to identify linked trends as a means of understanding the impacts of air pollution control in China. In most cities, the $PM_{2.5}$−NO_2 correlation coefficients were higher than the $PM_{2.5}$−SO_2 correlation coefficients, and the gap tended to expand as air quality improved. Multiple linear regression also indicated that $PM_{2.5}$ concentrations were more sensitive to changes in NO_2 than in SO_2. The rate of decrease in the $PM_{2.5}$ concentration with a decreasing NO_2 concentration is nearly 3 times higher than that with SO_2. These results support the priority of controlling NO_x to further reduce $PM_{2.5}$ pollution in China. The chemistry behind this was twofold: (1) NO_x can be converted into nitrate, and (2) NO_x contributes to atmospheric oxidation capacity. The decrease in $PM_{2.5}$ concentration always coincided with an increase in O_3 concentration when the $PM_{2.5}$ concentration was higher than 50 $\mu g\ m^{-3}$. However, the correlation between $PM_{2.5}$ and O_3 tended to change from negative to positive as air quality improved, indicating O_3 and $PM_{2.5}$ control could both benefit from reducing the concentrations of gas precursors.



INTRODUCTION

Along with rapid social and economic development in recent years, high concentrations of fine particulate matter ($PM_{2.5}$) have been observed in many areas of China, resulting in frequent haze events.[1] Due to the adverse effects of atmospheric particles on human health and visibility,[2,3] as well as their important role in the global climate,[4] controlling $PM_{2.5}$ pollution is an urgent issue in China.[1,5] In September 2013, the state council released a clean air action plan and set goals to reduce the five-year $PM_{2.5}$ concentrations in the Beijing−Tianjin−Hebei (BTH), Yangtze River delta (YRD), and Pearl River delta (PRD) areas by 25%, 20%, and 15%, respectively. Furthermore, local governments began taking action toward stricter emission standards in thermal power plants, industries, on-road vehicles, and other sources to reduce emissions of both gaseous pollutants and primary particulate matter.[6]

Many studies have reported improvements in eastern China's air quality in the past five years[7−9] due to both meteorological conditions[7,8] and emission control.[7,9] In addition to the 30−50% decrease in annual mean $PM_{2.5}$ across China over the period of 2013−2018,[8] some gaseous pollutants, such as SO_2,[7] have also shown a decreasing trend, although others, such as NH_3[10] and O_3,[11] have increased. Emission inventory studies have reported a consistent change in the corresponding pollutants. For example, Zheng et al.[6] estimated a relative change in China's anthropogenic emissions over the period of 2010−2017 of −62% for SO_2, −17% for NO_x, +11% for non-methane volatile organic compounds (NMVOCs), +1% for NH_3, and −27% for CO. These different rates of change have resulted in the transformation of the particle composition. For instance, Beijing has experienced a rapid transition from sulfate- to nitrate-dominated aerosol pollution during the winter,[12] thus highlighting the urgency of controlling NO_x in Beijing.

Secondary atmospheric processes are the main source of $PM_{2.5}$ mass in China.[1,13] During haze events, high concentrations (≥100 ppb) of SO_2, NO_x, NH_3, and volatile organic compounds (VOCs) have been detected.[14−17] As such, synergistic and/or antagonistic effects between pollutants may lead to complex nonlinear relationships between secondary aerosols and their precursors.[18−20] As an example of potential complex interactions, prior studies suggest that

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NO_x not only transforms into nitrate and alters the physicochemical properties of particles[21] but also can enhance sulfate[18,20] and contribute to secondary organic aerosol production,[22,23] resulting in a strong correlation between $PM_{2.5}$ and NO_2 concentration during haze events.[18] Analyzing these relationships should improve our understanding of air pollution under different conditions and in different regions and help in the formulation of more effective air pollution control strategies. Here, data from the China National Environmental Monitoring Center (CNEMC) and our observations at more rural sites were analyzed to determine the correlations between $PM_{2.5}$ and key gaseous pollutants, with resulting implications for air pollution control in China.

MATERIALS AND METHODS

Monitoring Network. Established by the Ministry of Ecology and Environment of China (MEE), the China National Environmental Monitoring Center (CNEMC) network (http://106.37.208.233:20035/) began measuring surface $PM_{2.5}$, PM_{10}, SO_2, NO_2, O_3, and CO concentrations in China in 2013. Both PM and trace gases are measured following the specifications and procedures for the ambient air quality continuous automated monitoring systems released by the MEE (HJ 653−2013 and HJ 654−2013). Details of these standards are listed on the MEE Web site: http://kjs.mee.gov.cn/hjbhbz/bzwb/jcffbz/201308/t20130802_256852.shtml (2019-08-18) and http://kjs.mee.gov.cn/hjbhbz/bzwb/jcffbz/201308/t20130802_256853.shtml (2019-08-18). $PM_{2.5}$ and PM_{10} mass concentrations are measured using oscillating microbalance and/or β absorption. SO_2 concentrations are measured by ultraviolet (UV) fluorescence. CO and O_3 concentrations are measured using infrared and UV absorption, respectively. NO_2 concentrations are measured by a molybdenum converter and chemiluminescence. Beginning with measurements in 114 cities in 2013, this network now includes 1656 sites in 378 cities. In this study, hourly data from 2013 to 2018 from the CNEMC network were used. When we analyzed the year-to-year variations, only the first 114 cities with measurements from 2013 were included.

In addition to the data from the CNEMC monitoring network (mostly in urban areas), observations in rural areas in 2018 were also used to study the correlations between $PM_{2.5}$ and trace gases. Thus, we also measured particle mass ($PM_{2.5}$ and PM_{10}) and trace gas (SO_2, CO, O_3, and NO_2) concentrations in 373 rural sites in Tangshan, Shijiazhuang, and Jincheng following the air quality continuous automated monitoring system (XHAQMS3000, Sailhero Co., Ltd.) standards of the MEE.

Data Quality Control. Data quality control methods similar to those of previous studies[24,25] were used here to reduce errors in the CNEMC monitoring network data set. First, zero or negative concentrations were set as missing. Second, extreme outlier concentrations were deleted (i.e., SO_2 > 1428 $\mu g\ m^{-3}$, NO_2 > 1026 $\mu g\ m^{-3}$, CO > 62.5 mg m^{-3}, $PM_{2.5}$ > 10000 $\mu g\ m^{-3}$, PM_{10} > 10000 $\mu g\ m^{-3}$, and O_3 > 1071 $\mu g\ m^{-3}$). Third, identical data repeated three or more times, which were likely to be duplicated by the reporting system of the monitoring network due to communication error,[26] were also set as missing, except for the first value. Fourth, temporally inconsistent outliers were removed following the method of Wu et al.[24]

Analysis Software and Methods. After data quality control, the hourly data matrix of the entire CNEMC data set was imported into MATLAB (MathWorks, Inc., ver. R2019b). Pearson correlation coefficients were obtained with the function "corrcoef". Multiple linear regression was performed with the function "regress" at the 0.05 significance level. The regression coefficients between $PM_{2.5}$ and gas precursors were the estimated coefficients for multiple linear regression of the responses in the $PM_{2.5}$ vector on the predictors in a matrix with three vectors, i.e., SO_2, NO_2, and CO.

RESULTS AND DISCUSSION

Changing Air Quality in China. Air pollutant concentrations changed markedly in China from 2013 to 2018. Based on mean values of 114 cities, the concentrations of CO, SO_2, $PM_{2.5}$, and PM_{10} decreased by 0.07 mg m^{-3} $year^{-1}$, 5 $\mu g\ m^{-3}$ $year^{-1}$, 6 $\mu g\ m^{-3}$ $year^{-1}$, and 7 $\mu g\ m^{-3}$ $year^{-1}$, respectively (Figure S1). Compared to levels in 2013, the concentrations of CO, SO_2, NO_2, $PM_{2.5}$, and PM_{10} in 2018 decreased by 37%, 71%, 19%, 45%, and 37%, respectively, while the NO_2 concentration decreased by only 19% in 2018 compared to 2013 and fluctuated from 2014 to 2018. In contrast, the O_3 concentration increased by 2.1 $\mu g\ m^{-3}$ $year^{-1}$, resulting in an increase of 17% from 2013 to 2018. The sum of NO_2 and O_3 also increased from 2014 to 2018 (Figure S1). O_3 and $PM_{2.5}$ are the two main pollutants exceeding air quality standards in China (particularly in the North China Plain, Fenwei Plain, and Sichuan Basin, as shown Figure S2), and both are largely dependent on NO_x concentrations. Furthermore, although the concentrations of SO_2 in most cities of China have declined recently, the levels of NO_x have shown minimal decreases in the past six years.

Correlations between $PM_{2.5}$ and Gaseous Pollutants in China. Significant correlations were found between $PM_{2.5}$ and gaseous pollutants (CO, NO_2, and SO_2) over the past six years in China (Figure S3). Meteorological conditions played essential roles in air pollution. Unfavorable dispersion conditions or regional pollution transportation usually causes simultaneous increases in the levels of all air pollutants and results in universal correlations between $PM_{2.5}$ and gas pollutants. In addition, air pollutants may also be correlated due to their common emission sources and related atmospheric chemical processes. However, due to the fact that different gas precursors were involved in different chemical reactions and contributed to secondary $PM_{2.5}$ differently, $PM_{2.5}$ might be correlated with different gas pollutants to different degrees, which is the research emphasis of this study, while the meteorological effect on the correlations of air pollutants will be investigated in future studies. As almost all combustion sources emit CO, significant correlations between $PM_{2.5}$ and CO were expected due to the contribution of combustion to most gaseous precursors of secondary $PM_{2.5}$, such as NO_x, SO_2, and anthropogenic VOCs. Because of this, we did not dedicate much effort to analyzing the correlation between $PM_{2.5}$ and CO in this study. The correlation found between $PM_{2.5}$ and SO_2 supports the results of prior studies, which reported that coal combustion is an important contributor to $PM_{2.5}$.[27,28] The correlation between $PM_{2.5}$ and NO_2 indicates that vehicle emissions are another important contributor, as most of the observation sites in the CNEMC network are in urban areas where NO_x is predominantly from mobile sources.

Higher correlations between $PM_{2.5}$ and gaseous pollutants were observed in the more polluted regions than in less polluted regions. In areas that experience heavy air pollution,

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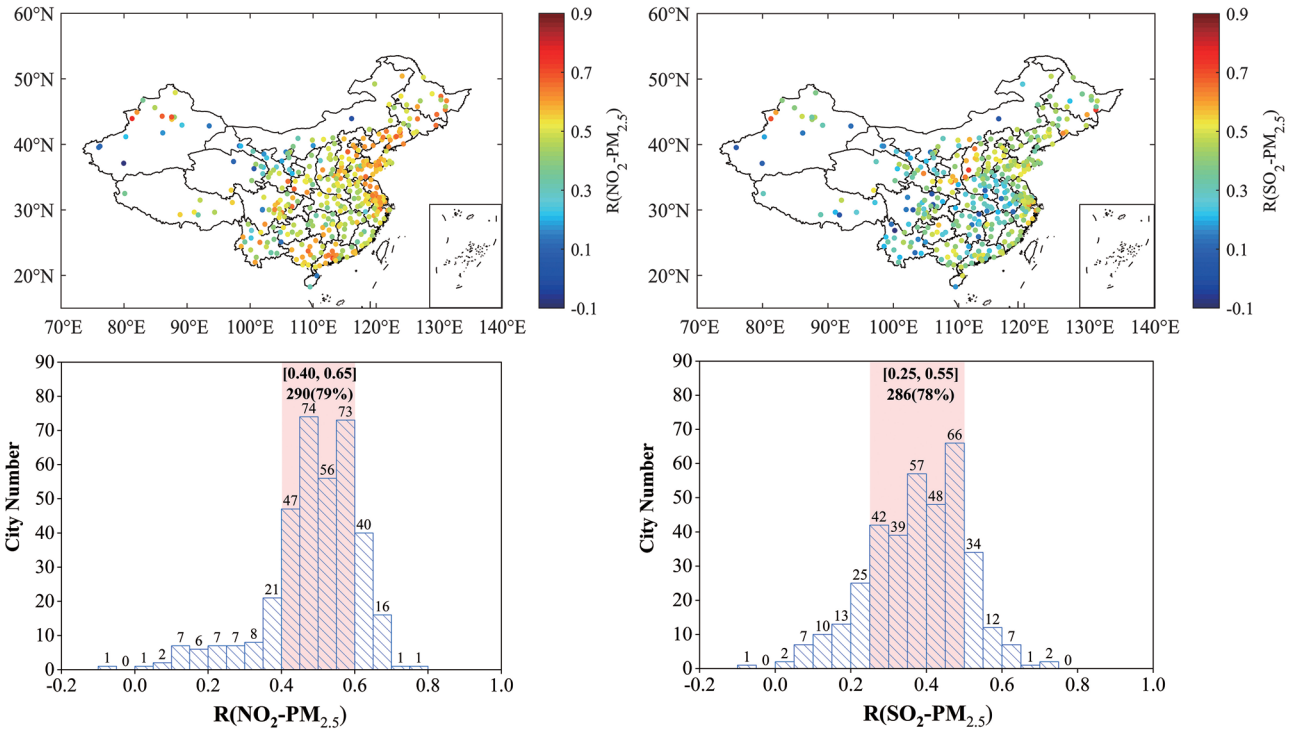

Figure 1. Pearson correlation coefficients between $PM_{2.5}$ and gaseous pollutants (NO_2 and SO_2) in China in 2018.

Table 1. Regression Coefficients between $PM_{2.5}$ and Gaseous Pollutants (uncertainties shown in parentheses)

year	α for SO_2	β for NO_2	γ for CO	δ	no. of data sets
2013–2018	0.17 ($\pm 3 \times 10^{-4}$)	0.59 ($\pm 5 \times 10^{-4}$)	0.022 ($\pm 2 \times 10^{-5}$)	4.4 ($\pm 2 \times 10^{-2}$)	5.1×10^7 (all of China)
2013	0.21 ($\pm 1 \times 10^{-3}$)	0.71 ($\pm 2 \times 10^{-3}$)	0.022 ($\pm 6 \times 10^{-5}$)	3.9 ($\pm 1 \times 10^{-1}$)	4.2×10^6 (114 cities)
2014	0.16 ($\pm 8 \times 10^{-4}$)	0.62 ($\pm 1 \times 10^{-3}$)	0.021 ($\pm 4 \times 10^{-5}$)	6.8 ($\pm 6 \times 10^{-2}$)	4.7×10^6 (114 cities)
2015	0.15 ($\pm 1 \times 10^{-3}$)	0.56 ($\pm 2 \times 10^{-3}$)	0.021 ($\pm 6 \times 10^{-5}$)	8.2 ($\pm 9 \times 10^{-2}$)	4.0×10^6 (114 cities)
2016	0.17 ($\pm 1 \times 10^{-3}$)	0.51 ($\pm 1 \times 10^{-3}$)	0.026 ($\pm 5 \times 10^{-5}$)	−0.50 ($\pm 6 \times 10^{-2}$)	5.1×10^6 (114 cities)
2017	0.14 ($\pm 1 \times 10^{-3}$)	0.48 ($\pm 2 \times 10^{-3}$)	0.031 ($\pm 6 \times 10^{-5}$)	−3.4 ($\pm 7 \times 10^{-2}$)	3.9×10^6 (114 cities)
2018	0.12 ($\pm 1 \times 10^{-3}$)	0.44 ($\pm 2 \times 10^{-3}$)	0.031 ($\pm 6 \times 10^{-5}$)	−1.2 ($\pm 5 \times 10^{-2}$)	4.9×10^6 (114 cities)

such as the substantially developed BTH, YRD, and PRD regions with high population densities, positive correlations were observed between $PM_{2.5}$ and NO_2 (Figure 1). The correlation between $PM_{2.5}$ and NO_2 was higher than that between $PM_{2.5}$ and SO_2 in 311 cities in 2018, accounting for ~85% of the total number of cities. The limited number of cities with correlation coefficients between $PM_{2.5}$ and NO_2 lower than that between $PM_{2.5}$ and SO_2 were mainly in northwestern China (Figure S4). In addition, a relatively higher correlation coefficient between $PM_{2.5}$ and SO_2 was also observed in the YRD region. These phenomena may indicate a relatively larger contribution of SO_2 emission (such as coal burning, ocean shipping, etc.) to $PM_{2.5}$ in these regions than in other places of China. In ~80% of the cities, the correlation coefficients between $PM_{2.5}$ and NO_2 ranged from 0.40 to 0.65, while the correlation coefficients between $PM_{2.5}$ and SO_2 ranged from 0.25 to 0.55. These results were consistent with the fact that the concentration of $PM_{2.5}$ and NO_x had synchronous variations, while the SO_2 concentration showed different time series profiles during the high-pollution episodes, as reported in our previous studies.[18,20] Furthermore, the gap between these two correlation coefficients increased as the level of pollution decreased. The correlation between $PM_{2.5}$ and NO_2 became more significant and higher than that between $PM_{2.5}$ and SO_2 as the level of air pollution decreased from BTH in the north to PRD in the south[29] (Figure S5), or from urban sites to more rural areas (Figure S6). The correlation between $PM_{2.5}$ and NO_2 for the 114 cities did not exhibit an obvious temporal trend, whereas the correlation between $PM_{2.5}$ and SO_2 tended to decrease in most cities from 2015 to 2018 (Figure S7). These phenomena may result from the increasing relative contribution of NO_2 to $PM_{2.5}$ due to the less efficient control of NO_x than SO_2 in the past decade in China. Thus, the relatively higher correlation between $PM_{2.5}$ and NO_x than with other pollutants highlights the need to prioritize the control of NO_x to reduce fine particle pollution in China.

Multiple Linear Regression Analysis of $PM_{2.5}$ and Gaseous Pollutants. On the basis of their linear correlations, we conducted multiple linear regression analyses between $PM_{2.5}$ and gaseous pollutants to determine the sensitivities of $PM_{2.5}$ to these pollutants. The regression model was designed as follows:

$$PM_{2.5} = \alpha \times SO_2 + \beta \times NO_2 + \gamma \times CO + \delta$$

Judging from the obtained regression coefficients (Table 1; P values and other statistical parameters of regression in Table S1), $PM_{2.5}$ appears to be more sensitive to NO_2 than to SO_2. The coefficient for NO_2 (β) was at least 3 times higher than that for SO_2 (α), which cannot be mathematically explained by

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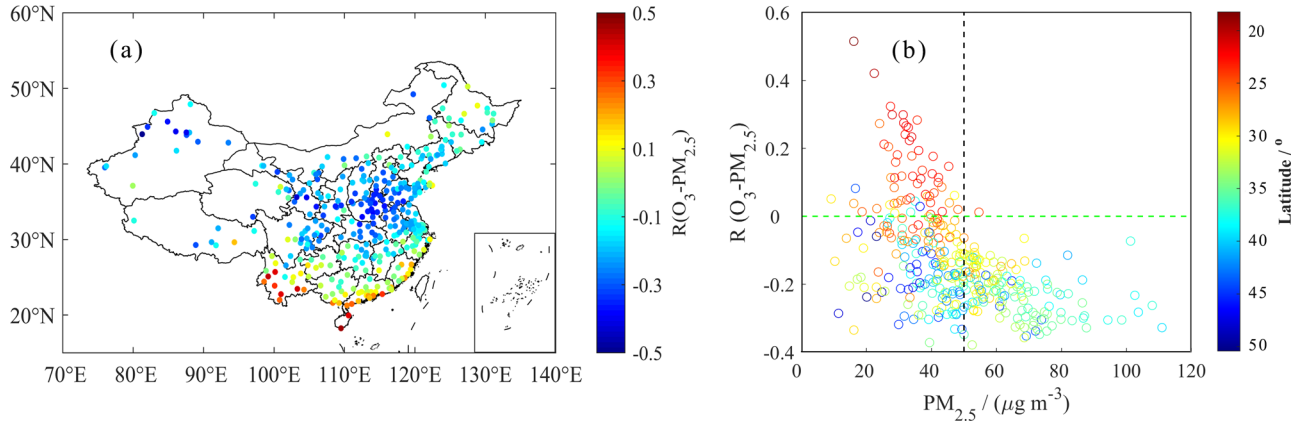

Figure 2. Correlation coefficients between $PM_{2.5}$ and O_3 in China (2013−2018).

the relative abundances of nitrate and sulfate in $PM_{2.5}$ or the nitrate/NO_2 and sulfate/SO_2 mass conversion ratios. These multiple linear regression analyses of $PM_{2.5}$ and gaseous pollutants indicated that a reduction of 1 $\mu g\ m^{-3}$ NO_2 reduced $PM_{2.5}$ by more than 0.5 $\mu g\ m^{-3}$, whereas a reduction of 1 $\mu g\ m^{-3}$ SO_2 reduced $PM_{2.5}$ by less than 0.2 $\mu g\ m^{-3}$. We also observed a decreasing trend in the coefficients over time for NO_2 and SO_2, but an increasing trend for CO. These trends indicate that non-point emission sources, such as biomass burning, which emits a large amount of CO, may contribute a higher proportion to $PM_{2.5}$ under stricter control of SO_2 and NO_x in power plants and mobile sources.

Possible Reasons for the High Correlation between $PM_{2.5}$ and NO_2. Various chemical mechanisms for explaining the key roles of NO_2 in complex air pollution have been hypothesized and supported by field and laboratory studies.[18,30,31] As indicated in previous studies, NO_x contributes to secondary $PM_{2.5}$ by forming nitrate directly and by enhancing aerosol-phase oxidation indirectly.[18,32] On one hand, an increasing proportion of nitrate has been observed in $PM_{2.5}$ in eastern Chinese cities.[12,33] On the other hand, NO_x was reported to contribute to oxidation capacity during secondary aerosol formation as a catalyst in heterogeneous processes,[18,20] and as oxidants in aqueous reactions.[30,34−36] Under the complex air pollution conditions in China, interface reactions related to NO_x have become important due to the high concentrations of aerosol and NH_3[18,30,34,36] and lead to the "explosive" growth of secondary aerosols during severe haze episodes in China.[18,30] In Figure S8, the correlation coefficients between $PM_{2.5}$ and NO_2 were higher in the winter and autumn seasons, with higher pollution levels than that during summer and spring when the air is cleaner. In Figure S9, a higher correlation was found between $PM_{2.5}$ and NO_2 during heavy pollution accumulation periods than during other periods, indicating the existence of active NO_x-related secondary aerosol processes during accumulation. These chemical mechanisms resulted in the key roles of NO_x in the formation of secondary $PM_{2.5}$ and explained why $PM_{2.5}$ is highly related and very sensitive to NO_2 in China.

Secondary $PM_{2.5}$ is the main reason for haze pollution in China,[1,13] with SO_2, NO_x, NH_3, and VOCs being key precursors.[14−17] At present, SO_2 has been brought under effective control with universal desulfurization in coal-fired power plants across the country.[6] The economic costs for further substantial decreases in SO_2 emissions will be huge. Both VOCs and NH_3 are derived from a wealth of sources, with a lack of effective control methods relative to NO_x.[6,10] These situations, and the results of this study, highlight the need to prioritize the control of NO_x to further reduce fine particle pollution in China.

The "Seesaw" Relationship between $PM_{2.5}$ and O_3 in China. The increase in the O_3 concentration in China in the past several years can be partially explained by the reduction of particles,[11] which results in less heterogeneous HO_2 radical loss and higher actinic flux. As indicated in Figure 2, there was an obvious south−north distribution for correlation coefficients between $PM_{2.5}$ and O_3. $PM_{2.5}$ and O_3 are negatively related in north China but become positively related in south China. In addition, there was an obvious seasonal variation in that $PM_{2.5}$ and O_3 tend to be more positively correlated in the summer but tend to be more negatively correlated in the winter (Figure S10). One speculative reason for this phenomenon is that $PM_{2.5}$ does not reduce actinic flux and HO_2 radical significantly due to sufficient solar irradiation and a relatively low concentration of $PM_{2.5}$ in south China or in the summer. $PM_{2.5}$ and O_3 tend to be positively correlated possibly due to their common precursors, such as VOCs and NO_x, and their simultaneous generation in photochemical reactions. According to Figure 2b, the decrease in $PM_{2.5}$ concentration always coincided with an increase in O_3 concentration in areas where the $PM_{2.5}$ concentration was higher than 50 $\mu g\ m^{-3}$. However, the correlation between $PM_{2.5}$ and O_3 became less negative when the $PM_{2.5}$ concentration decreased. In south China, where $PM_{2.5}$ concentrations are close to the national air quality standard, such as PRD, $PM_{2.5}$ and O_3 were positively correlated, and therefore, O_3 pollution control is also expected to benefit from the emission reduction of gas precursors as $PM_{2.5}$.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.estlett.0c00403.

Temporal variation and spatial variation of air pollutants (Figures S1 and S2), Pearson correlation coefficients between air pollutants in China, different regions, and urban versus country sites (Figures S3−S6), correlation coefficients in different years, seasons, and pollution periods (Figures S7−S10), and statistical parameters of the regression between $PM_{2.5}$ and gaseous pollutants (Table S1) (PDF)

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Notes

The authors declare no competing financial interest.

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