Correlations between PM$_{2.5}$ and Ozone over China and Associated Underlying Reasons

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Abstract: We investigated the spatial-temporal characteristics of the correlations between observed PM$_{2.5}$ and O$_3$ over China at a national-scale level, and examined the underlying reasons for the varying PM$_{2.5}$–O$_3$ correlations by using a chemical transport model. The PM$_{2.5}$ concentrations were positively correlated with O$_3$ concentrations for most regions and seasons over China, while negative correlations were mainly observed in northern China during winter. The strongest positive PM$_{2.5}$–O$_3$ correlations with correlation coefficients ($r$) larger than $+0.7$ existed in southern China during July, and the strongest negative correlations ($r < -0.5$) were observed in northern China during January. It was a very interesting phenomenon that the positive PM$_{2.5}$–O$_3$ correlations prevailed for high air temperature samples, while the negative correlations were generally found in cold environments. Together, the effective inhibitory effect of PM$_{2.5}$ on O$_3$ generation by reducing photolysis rates and the strong titration effect of freshly emitted NO with O$_3$ contributed to the strongest negative PM$_{2.5}$–O$_3$ correlations in northern China during January (i.e., in cold environments). The strongest positive correlations in southern China during July (i.e., at high temperature), however, were mainly attributed to the promoting effect of high O$_3$ concentration and active photochemical activity on secondary particle formation.

Keywords: PM$_{2.5}$; ozone; correlation; temperature

1. Introduction

Fine particulate matter with a diameter of 2.5 $\mu$m or less (PM$_{2.5}$) is an important pollutant in the atmosphere. Epidemiological studies have revealed a robust correlation between PM$_{2.5}$ levels and the morbidity of cardiovascular and respiratory diseases $^{[1,2]}$. In addition, PM$_{2.5}$ has strong extinction abilities, and therefore, reduces atmospheric visibility and affects traffic safety $^{[3,4]}$. Tropospheric ozone (O$_3$), as another air pollutant, has adverse effects on human health, ecosystems, and crop growth $^{[5–8]}$.

At present, haze and ozone pollution are the most serious atmospheric environmental problems in China $^{[9–16]}$. However, the formation reasons for the complex air pollution characterized by PM$_{2.5}$ and O$_3$ are very complex. Although the two important pollutants have different formation mechanisms, the interactions between them lead to close connections and relations. The complex physical and
The chemical properties of PM$_{2.5}$ may affect the generation and loss of O$_3$ [12,17], while O$_3$ may influence atmospheric oxidizing capacity, and therefore, affect the formation of secondary PM$_{2.5}$ [18,19]. The interactions between PM$_{2.5}$ and O$_3$ lead to certain correlations of observed concentrations; however, the observed correlations may vary in different seasons and different regions [20–25]. Revealing the rules for PM$_{2.5}$–O$_3$ correlations over China, as well as investigating the underlying reasons/mechanisms for the PM$_{2.5}$–O$_3$ correlations, is the scientific basis and an essential requirement for the coordinated control of complex air pollution.

The PM$_{2.5}$ may reduce O$_3$ concentrations by altering the photolysis rate. The main components of PM$_{2.5}$, such as sulfate, nitrate, black carbon, and organic carbon, can scatter and absorb solar radiation directly, and can also alter the optical properties and life cycle of clouds by becoming cloud condensation nuclei, which in turn, decrease the intensity of incident ultraviolet radiation and finally reduce the photolysis rate and O$_3$ generation [26–31]. Li et al. [29] investigated the impact of particulates on O$_3$ via changing photolysis frequencies and reported that the boundary layer O$_3$ below 1 km was reduced by 5.4% over central Eastern China in June 2006. A high O$_3$ concentration indicates a strong atmospheric photochemical reactivity, which can promote the formation of secondary particles [19,32–35]. By analyzing concentrations of PM$_{2.5}$, its compositions and gas pollutants measured at a rural site (Dian Shan Lake supersite) in the eastern Yangtze River Delta from 23 July to 11 August 2013, Wang et al. [19] found that strong correlations existed between solar radiation and the production rate of sulfate by gas-phase oxidation, between day-time nitrate and nitrogen dioxide (NO$_2$) and O$_3$, and between secondary organic aerosol (SOA) and O$_x$ (O$_3$+NO$_2$), which indicated that the formation of secondary particles (sulfate, nitrate, and SOA) was promoted by photochemical oxidation.

Certain correlations between PM$_{2.5}$ and O$_3$ were reported in several cities of China, and the observed PM$_{2.5}$–O$_3$ correlations varied in different seasons and different regions [20–25,36–39]. Xu et al. [36] analyzed observed pollutant concentrations in Beijing and reported that PM$_{2.5}$ concentrations were negatively correlated with O$_3$ concentrations with a correlation coefficient ($r$) of $-0.51$ in February 2003, but no statistically significant correlations were found in August 2003. By analyzing the observed pollutant concentrations provided by Shanghai Environment Monitoring Center, Shi et al. [38] revealed that PM$_{2.5}$ concentrations were positively correlated ($r = +0.59$) with O$_3$ concentrations during ozone-rich days in July and August 2013.

Previous studies revealed correlations between surface-layer PM$_{2.5}$ and O$_3$ concentrations over China. However, these studies mostly focused on the individual city and season, which could not make clear representative sense for comprehensively understanding the PM$_{2.5}$–O$_3$ correlations over the whole of China. Furthermore, most of these studies only mentioned the relevant phenomenon, while the reasons for the PM$_{2.5}$–O$_3$ correlations have been poorly understood. Although some studies revealed interactions between PM$_{2.5}$ and O$_3$, the impacts of PM$_{2.5}$–O$_3$ interactions on their correlations, especially the importance of different interactions in different regions and seasons, are still unclear and need to be further investigated.

This paper aimed to (1) obtain the spatial-temporal characteristics of the correlations between PM$_{2.5}$ and O$_3$ at a national-scale level, based on the pollutant concentrations measured at all monitoring sites of China for the whole year 2016, and (2) examine the underlying mechanisms on the varying PM$_{2.5}$–O$_3$ correlations in different regions and seasons using a chemical transport model (GEOS-Chem). The obtained knowledge is expected to provide a scientific basis for the coordinated control of complex air pollution over China. The methods, including descriptions of in situ measurements, data analysis, and model configuration are presented in Section 2. Section 3 shows the results, including observed PM$_{2.5}$–O$_3$ correlations, model evaluation, and underlying reasons/mechanisms. The conclusion and discussion are presented in Section 4.
2. Methods

2.1. In Situ Measurements and Data Analysis

The Ministry of Ecological and Environment (MEE), formerly the Ministry of Environmental Protection of the People’s Republic of China (MEP), has begun to release to the public the real-time monitoring air quality data of six criteria pollutants including PM$_{2.5}$ and O$_3$ covering most cities in China since 2013. The observation sites in each city are designed as a mix of urban and background sites, with most of the sites located in urban areas. According to China’s Environmental Protection Standards, the $\beta$ absorption method and the micro oscillating balance method are used to continuously measure PM$_{2.5}$ concentrations (“HJ 653-2013”), while the ultraviolet spectrophotometry method is used to automatically monitor O$_3$ concentrations (“HJ 654-2013”).

The hourly PM$_{2.5}$ and O$_3$ concentrations can be obtained from the MEE website, from which we downloaded the concentrations at 1497 sites of the whole China for year 2016. For each site, the negative or missing values were removed; those sites with less than 80% valid data were also abandoned. Although the MEE provides hourly PM$_{2.5}$ and O$_3$ concentrations, the National Ambient Air Quality Standards (NAAQS, GB3095-2012) sets limits on annual or daily mean concentrations for PM$_{2.5}$ and maximum daily 8 h average (MDA8) or hourly mean concentrations for O$_3$. For consistency, we calculated daily mean PM$_{2.5}$ concentration and daily MDA8 O$_3$ concentration to conduct correlation analysis. Following the NAAQS, we conducted the validity treatment for data statistics as follows: the daily average PM$_{2.5}$ concentrations were calculated when there were valid data for more than 20 h during that day; the 8 h average O$_3$ concentrations were calculated when there were valid data for at least 6 h for every 8 h. Pearson correlation coefficients ($r$) were calculated for correlation analysis.

The meteorological data of surface temperature over China for the year 2016, which will be used in Section 3.1 to examine the temperature dependence of PM$_{2.5}$–O$_3$ correlations, were extracted from the re-analysis dataset of the ERA-Interim in the European Centre for Medium-Range Weather Forecasts (ECMWF) [40]. These gridded observation records with a horizontal resolution of $0.25^\circ \times 0.25^\circ$ were then bilinearly interpolated to the corresponding air quality monitoring stations, as was done in Wang et al. [41] and Zhong et al. [42].

2.2. Model Configuration

To investigate the reasons for the varying PM$_{2.5}$–O$_3$ correlations in different regions and seasons, we needed to obtain concentrations of PM$_{2.5}$ components, photolysis rates, etc., at all sites over China for the year 2016, which were almost unavailable from in situ measurements. Therefore, a chemical transport model (GEOS–Chem) was used to reproduce the observed PM$_{2.5}$–O$_3$ correlations and examine the underlying mechanisms. It was easy to output concentrations of PM$_{2.5}$ components, photolysis rates, and other variables for the chemical transport model.

The simulations of PM$_{2.5}$ and O$_3$ were carried out with the nested-grid version of the GEOS-Chem model, which included detailed ozone–NO$_x$–VOC–aerosol chemistry [43], with a horizontal resolution of $0.5^\circ$ latitude $\times 0.625^\circ$ longitude (version 11-01). The nested domain was set over Asia ($60^\circ$–$150^\circ$ E, $11^\circ$ S–$55^\circ$ N), and the chemical boundary conditions that were updated every 3 h were provided by the global GEOS-Chem simulation with $2^\circ$ latitude $\times 2.5^\circ$ longitude resolution. The simulation was driven by the assimilated MERRA-2 meteorological data from the Goddard Earth Observing System (GEOS) of the NASA Global Modeling Assimilation Office (GMAO) [44]. Over the Asian domain, MIX 2010 was taken as the baseline anthropogenic inventory [45], and the scaling factors after year 2010 followed Zheng et al. [46]. The biomass burning emissions were taken from the Global Fire Emissions Database (GFED4) [47]. Natural emissions, including NO$_x$ from lighting and soil and VOCs from vegetation, were calculated on the basis of MERRA-2 meteorological parameters. The GEOS-Chem simulation was conducted from 1 January to 31 December of the year 2016 after a 6 month model spin-up.
3. Results

3.1. Observed PM$_{2.5}$–O$_3$ Correlations

Figure 1 shows the spatial-temporal distributions of correlations between daily PM$_{2.5}$ and MDA8 O$_3$ concentrations over China. Each panel represents each month for the year 2016. It is too intensive to display all 1497 sites on the map, therefore, we present the correlations for all 360 cities. The PM$_{2.5}$ concentrations were positively correlated with O$_3$ concentrations for most regions and seasons over China, while the negative correlations mainly existed in northern China during winter. The strongest positive correlations ($r > +0.7$) were observed in southern China during July, and the strongest negative correlations ($r < -0.5$) were observed in northern China during January, with most cities passing the 95% confidence level.

![Figure 1](image-url)

Figure 1. Spatial-temporal distributions of correlations between observed daily PM$_{2.5}$ and maximum daily 8 h average (MDA8) O$_3$ concentrations over China. Each panel represents each month for the year 2016. The dots with crosses are statistically significant at the 95% level.

Interestingly, the spatial-temporal distributions of PM$_{2.5}$–O$_3$ correlations highly resembled those of temperature (shown in Figure S1). Both the PM$_{2.5}$–O$_3$ correlations and temperature reached the maximum in southern China during July and reached the minimum in northern China during January. To further investigate the relations between PM$_{2.5}$–O$_3$ correlations and temperature, we provide scatter plots of daily PM$_{2.5}$ and MDA8 O$_3$ concentrations color coded with temperature for all cities of the whole China during 2016 in Figure 2a. Regularly, a positive correlation between PM$_{2.5}$ and O$_3$ was found for high air temperature samples, while a negative correlation prevailed in cold environments. The phenomenon can be presented more clearly when the data points are separated into northern cities (shown in Figure 2b) and southern cities (shown in Figure 2c). A remarkable positive correlation was...
found for high temperature over southern China and a significant negative correlation was observed for low temperature over northern China, which was also well reflected in Figure 1. It was noted that the relations between PM$_{2.5}$–O$_3$ correlations and other meteorological parameters (e.g., relative humidity) were much weaker (scatter plots for other meteorological parameters were not shown).

Figure 2. Scatter plots of observed daily PM$_{2.5}$ and MDA8 O$_3$ concentrations color coded with temperature for all cities of the (a) whole China, (b) northern China, and (c) southern China during the year 2016. Northern (southern) China is defined as the area north (south) of 33° N.

In the following sections, we focus on comparing data points which exhibit the strongest positive PM$_{2.5}$–O$_3$ correlations and high air temperature (i.e., southern China in July) and those that exhibit the strongest negative PM$_{2.5}$–O$_3$ correlations and low air temperature (i.e., northern China in January), to investigate the underlying reasons for the varying PM$_{2.5}$–O$_3$ correlations.

3.2. Model Evaluation

Previous studies have indicated that the GEOS-Chem model captures the distributions of observed PM$_{2.5}$ [13,48,49] and O$_3$ [11,50–52] over China fairly well. We conducted comparisons with the MEE measurements here to evaluate whether the version of the GEOS-Chem model used in this study can reproduce the observed variations in surface-layer PM$_{2.5}$ and O$_3$ and their correlations.

The observed and simulated daily PM$_{2.5}$ and MDA8 O$_3$ concentrations for northern cities in January and southern cities in July are shown in Figures 3 and 4, respectively. Although the model generally underestimated (overestimated) the absolute PM$_{2.5}$ (MDA8 O$_3$) concentrations, the model successfully captured the temporal variations of PM$_{2.5}$ and MDA8 O$_3$ concentrations. For northern cities in January, the correlation coefficients between the simulated and observed PM$_{2.5}$ (MDA8 O$_3$) concentrations ranged from 0.70 to 0.87 (from 0.67 to 0.89); for southern cities in July, the correlation coefficients for PM$_{2.5}$ (MDA8 O$_3$) were in the range of 0.52 to 0.80 (0.79 to 0.92). For both observed and simulated concentrations, PM$_{2.5}$ presented an overall negative correlation with MDA8 O$_3$ in northern China during January but exhibited a significant positive correlation with MDA8 O$_3$ in southern China during July. The observed inverse correlations were reproduced by the GEOS-Chem model fairly well. Therefore, it was feasible to conduct PM$_{2.5}$–O$_3$ correlation analysis using the GEOS-Chem model.

3.3. Underlying Reasons and Mechanisms

As mentioned in the Introduction, there exist interactions between PM$_{2.5}$ and O$_3$. However, PM$_{2.5}$ and O$_3$ may exhibit varying and even inverse correlations in different seasons and different regions, which indicates that the importance of different interactions on the PM$_{2.5}$–O$_3$ correlations may vary over time across space. The Beijing–Tianjin–Hebei (BTH, 37°–41° N, 114°–118° E) agglomeration, as the representative of northern China, has a low temperature below 0 °C and the strongest negative PM$_{2.5}$–O$_3$ correlation in January. The Pearl River Delta (PRD, 22°–24° N, 112°–115° E) agglomeration,
as the representative of southern China, has a high temperature above 27 °C and the strongest positive PM$_{2.5}$–O$_3$ correlation in July. Therefore, in this section, we chose the BTH in January (as the representative of negative PM$_{2.5}$–O$_3$ correlations and low temperature) and PRD in July (as the representative of positive PM$_{2.5}$–O$_3$ correlations and high temperature), to compare the importance of different PM$_{2.5}$–O$_3$ interactions on the correlations for different regions and seasons (i.e., different temperature) and reveal the underlying reasons/mechanisms, based on the GEOS-Chem simulation.

Figure 3. Observed and simulated daily PM$_{2.5}$ and MDA8 O$_3$ concentrations for northern cities in January. Observed (simulated) concentrations are shown in dashed (solid) lines. The PM$_{2.5}$ (MDA8 O$_3$) concentrations are shown in black (red) lines. The correlation coefficient ($r$) and normalized mean bias (NMB) between the observations and simulations are shown above each panel.
Figure 4. Observed and simulated daily PM$_{2.5}$ and MDA8 O$_3$ concentrations for southern cities in July. Observed (simulated) concentrations are shown in dashed (solid) lines. The PM$_{2.5}$ (MDA8 O$_3$) concentrations are shown in black (red) lines. The correlation coefficient ($r$) and normalized mean bias (NMB) between the observations and simulations are shown above each panel.

3.3.1. PM$_{2.5}$ Suppressing O$_3$ Generation by Reducing Photolysis Rates

Particulates may decrease the actinic flux of incident solar radiation by scattering or absorbing solar radiation directly and altering the optical properties of clouds indirectly, and inhibit the photolysis reactions near the surface by reducing the photolysis rates, which finally reduce the O$_3$ generation [26–31].

Figure 5 shows the time-series of simulated daily PM$_{2.5}$ concentrations, solar radiation at the ground (RADSWG), photolysis rates (J(NO$_2$) and J(O$_3$)), and MDA8 O$_3$ concentrations, for BTH in January and PRD in July. It is remarkable in Figure 5a that the RADSWG was negatively correlated with PM$_{2.5}$ ($r = -0.45$), indicating the strong extinction effects of particulates on solar radiation. The photolysis rates, including J(NO$_2$) and J(O$_3$), and MDA8 O$_3$ concentrations presented significantly positive correlation with RADSWG, which finally resulted in a strongly negative correlation between PM$_{2.5}$ and MDA8 O$_3$ for BTH in January. Influenced by meteorological conditions, the PM$_{2.5}$ concentrations exhibited spikes and valleys. When the PM$_{2.5}$ concentrations reached the peaks, the RADSWG, photolysis rates, and MDA8 O$_3$ concentrations reached the lowest levels due to the inhibitory effect of PM$_{2.5}$ on O$_3$ generation by reducing photolysis rates. By contrast, for PRD in July (Figure 5b), the correlation between RADSWG and PM$_{2.5}$ was much smaller ($r = -0.27$), indicating a weaker extinction effect of particulates on solar radiation and a consequently weaker influence on
photolysis rates and MDA8 O\textsubscript{3} concentrations. For BTH in January, the average PM\textsubscript{2.5} concentrations were relatively high because of winter heating and low boundary layer height associated with low temperature, which led to a more effective suppressing effect of PM\textsubscript{2.5} on O\textsubscript{3} generation by reducing photolysis rates for cold environments. A similar phenomenon has also been reported by Tie et al. [26], who pointed out that surface photolysis rates J(NO\textsubscript{2}) and J(O\textsubscript{3}) in Eastern China were reduced by 10–30% and 20–30% due to the effect of particulates on photolytic radiation in winter, as well as 1–10% and 5–20% in summer, leading to reductions in surface O\textsubscript{3} concentrations by 2–4% in winter and less than 2% in summer. Overall, the negative PM\textsubscript{2.5}–O\textsubscript{3} correlation for cold environment may be partly attributed to the effective inhibitory effect of PM\textsubscript{2.5} on O\textsubscript{3} generation by reducing photolysis rates at low temperature.

![Figure 5](image-url)  
**Figure 5.** Time-series of simulated daily PM\textsubscript{2.5} concentrations, solar radiation at the ground (RADSWG), photolysis rates (J(NO\textsubscript{2}) and J(O\textsubscript{3})), and MDA8 O\textsubscript{3} concentrations for (a) Beijing–Tianjin–Hebei (BTH) in January and (b) Pearl River Delta (PRD) in July.

### 3.3.2. NO Suppressing O\textsubscript{3} Production through the NO Titration Effect

It is known that excessive NO is not favorable for O\textsubscript{3} generation. If NO levels are high, O\textsubscript{3} production is suppressed by the “O\textsubscript{3} + NO → NO\textsubscript{2} + O\textsubscript{2}” reaction, usually referred to as NO titration, which is an important O\textsubscript{3} removal process associated with freshly emitted NO [14,53].

The time-series of simulated daily PM\textsubscript{2.5}, BC, NO, and MDA8 O\textsubscript{3} concentrations, for BTH in January and PRD in July, are shown in Figure 6. The NO concentration was calculated to be 8.5 ppbv averaged over BTH in January, six times that for PRD in July. It is conspicuous, in Figure 6a, that the MDA8 O\textsubscript{3} was negatively correlated with NO with a high correlation coefficient of −0.74, indicating a
strong NO titration effect for BTH in January. When the NO concentrations reached the spikes, the MDA8 O₃ concentrations reached the valleys due to the strong NO titration effect. By contrast, the NO titration effect for PRD in July was weaker; the correlation coefficient between MDA8 O₃ and NO was −0.55. Ding et al. [20] and Chen et al. [25] also reported similar finding that the negative correlation mainly existed for low temperature data, suggesting a titration effect of freshly emitted NO with O₃ in cold seasons.

Figure 6. Time-series of simulated daily concentrations for PM₂.₅, black carbon (BC), NO, and MDA8 O₃ for (a) BTH in January and (b) PRD in July.

For BTH in January, the lower air temperature (generally indicating the feebler solar radiation) resulted in weaker atmospheric oxidation ability, therefore, more NO was freshly emitted. The BC, as a primary particulate, was difficult to generate or clear through chemical reactions. It is noted that NO and BC, as well as PM₂.₅, have similar sources, such as combustion and traffic activities [20,25]. Therefore, the freshly emitted NO presented a significant positive correlation with the primary particulate BC (r = 0.85) and consequently with PM₂.₅ (r = 0.73). In contrast, for PRD in July, more NO was converted to NO₂, and therefore, NO tended to be less correlated with the primary particulate BC (r = 0.39) and consequently with PM₂.₅ (r = −0.13) (Figure 6b).

In conclusion, the significant negative correlation between NO and MDA8 O₃, and the remarkable positive correlation between NO and PM₂.₅, led to the negative correlation between PM₂.₅ and MDA8 O₃ for BTH in January. The negative PM₂.₅–O₃ correlation at low temperature may be partly attributed to the strong titration effect of high NO concentration, which is consistent with primary PM₂.₅ in a cold environment.
3.3.3. High O₃ Concentration and Active Photochemical Activity Promoting Secondary PM₂.₅ Formation

As reported in previous studies, high O₃ concentration generally indicates strong atmospheric photochemical reactivity, which can promote the secondary particulate formation. For example, the photochemical oxidation of SO₂ to H₂SO₄ may be promoted by strong atmospheric photochemical reactions, and the formation of HNO₃ can be strongly enhanced by high O₃ [19,32].

To examine the effects of O₃ and photochemical activity on secondary particulate formation under different temperature conditions, we compared the time-series of simulated daily O₃ and MDA8 O₃ concentrations, SOR and NOR, as well as SNA and PM₂.₅ concentrations between BTH in January and PRD in July in Figure 7. The total oxidant Oₓ (Oₓ = O₃ + NO₂) was used to characterize the atmospheric oxidation capacity, following Wang et al. [14], Jia et al. [22], and Clapp and Jenkin [54]. The sulfur oxidation ratio, SOR = n-SO₄²⁻/(n-SO₄²⁻ + n-SO₂), was a measure of the conversion degree of sulfur; the nitrogen oxidation ratio, which was defined as NOR = n-NO₃⁻/(n-NO₃⁻ + n-NO₂), was used to quantitatively express the conversion degree of nitrogen [55–58]. The secondary inorganic particulate was defined as SNA = SO₄²⁻ + NO₃⁻ + NH₄⁺.

![Figure 7](image-url)  
**Figure 7.** Time-series of simulated daily total oxidant (Oₙ) and MDA8 O₃ concentrations, sulfur oxidation ratio (SOR) and nitrogen oxidation ratio (NOR), as well as secondary inorganic particles (SNA) and PM₂.₅ concentrations for (a) BTH in January and (b) PRD in July. The Oₓ = O₃ + NO₂, SOR = n-SO₄²⁻/(n-SO₄²⁻ + n-SO₂), NOR = n-NO₃⁻/(n-NO₃⁻ + n-NO₂), SNA = SO₄²⁻ + NO₃⁻ + NH₄⁺.

For PRD in July (Figure 7b), the correlation coefficient between MDA8 O₃ and Oₓ was 0.93, indicating the important role of O₃ on the atmospheric oxidizing capacity. The SOR (NOR) exhibited
a pronounced positive correlation with O₃, with a high correlation coefficient of 0.89 (0.93), which indicates that the formation of secondary inorganic particulates can be promoted by photochemical oxidation and O₃. Consequently, the SNA and PM₂.₅ were positively correlated with O₃ and MDA8 O₃ concentrations. It is noted that high concentrations of O₃ and strong atmospheric photochemical reactions may also enhance the formation of secondary organic aerosol (SOA) [19]. By analyzing concentrations of SOA and gas pollutants measured in the summer of 2013, Wang et al. [19] found that SOA had a good correlation with O₃, with a correlation coefficient of 0.90, which indicated that SOA formation was mainly promoted by photochemical oxidation. In contrast, the correlation between SOR (NOR) and O₃ was much smaller and even negative for BTH in January (Figure 7a). In general, high air temperature means strong solar radiation and high O₃ concentration. Therefore, the promoting effect of high O₃ concentration and active photochemical activity on secondary PM₂.₅ formation was more effective under high temperature conditions.

Overall, in an environment of high temperature, high concentration of O₃ indicates a strong atmospheric photochemical reactivity, and significantly promotes the level of atmospheric oxidation. The strong atmospheric oxidation capacity, in turn, enhances the formation of both secondary inorganic particulates and secondary organic particulates. The enhanced formation of secondary particulates eventually leads to significant positive PM₂.₅–O₃ correlation in a hot environment.

4. Conclusions and Discussion

In this study, the spatial-temporal characteristics of the correlations between PM₂.₅ and O₃ were investigated at the national-scale level, based on the pollutant concentrations measured at all monitoring sites in China from the Ministry of Ecological and Environment for the whole year of 2016. The underlying reasons or mechanisms on the varying PM₂.₅–O₃ correlations in different regions and seasons were examined by a chemical transport model (GEOS-Chem).

Measurements showed that the PM₂.₅ concentrations were positively correlated with O₃ concentrations for most regions and seasons over China, while the negative correlations were mainly observed in northern China during winter. The strongest positive PM₂.₅–O₃ correlations with correlation coefficients (r) larger than +0.7 existed in southern China during July, and the strongest negative correlations (r < −0.5) were observed in northern China during January.

It was very interesting to see that the spatial-temporal distributions of PM₂.₅–O₃ correlations highly resembled those of temperature. Therefore, the relations between PM₂.₅–O₃ correlations and temperature were further investigated. Regularly, the positive PM₂.₅–O₃ correlations prevailed for high air temperature samples, while the negative correlations were generally found in a cold environment.

We then focused on comparing data points which exhibited the strongest positive PM₂.₅–O₃ correlations and high air temperature (i.e., southern China in July) and those that exhibited the strongest negative PM₂.₅–O₃ correlations and low air temperature (i.e., northern China in January) to investigate the underlying reasons for the varying PM₂.₅–O₃ correlations for different regions and seasons (i.e., different temperature), based on the GEOS-Chem simulation. Model evaluations showed that it was viable and reliable to conduct PM₂.₅–O₃ correlation analysis using the GEOS-Chem model.

The PM₂.₅ may suppress O₃ generation by reducing photolysis rates. For northern China in January (i.e., low temperature condition), the average PM₂.₅ concentrations were relatively high, which led to a more effective inhibitory effect of PM₂.₅ on O₃ generation for cold environments than for hot environments. Therefore, the negative PM₂.₅–O₃ correlation for a cold environment may be partly attributed to the effective inhibitory effect of PM₂.₅ on O₃ generation by reducing photolysis rates at low temperature. The NO may suppress O₃ production through the NO titration effect, and the inhibitory effect was found to be stronger for low temperature conditions than for high temperature conditions. However, the freshly emitted NO presented a significant positive correlation with the primary particulate BC, and consequently, with PM₂.₅ in cold seasons. Therefore, the negative PM₂.₅–O₃ correlation at low temperature may also be partly attributed to the strong titration effect of high NO concentration, which was consistent with primary PM₂.₅ in a cold environment. High concentration
of O₃ generally indicates active photochemical activity, which may promote the secondary PM₂.₅ formation. In general, high O₃ concentration occurs in an environment of high temperature and strong solar radiation. Therefore, the positive PM₂.₅–O₃ correlation in a hot environment may be a result of the promoting effect of high O₃ concentration and active photochemical activity on secondary particle formation.

In conclusion, the effective inhibitory effect of PM₂.₅ on O₃ generation by reducing photolysis rates at low temperature, and the strong titration effect of freshly emitted NO with O₃ in cold seasons, together contribute to the strongest negative PM₂.₅–O₃ correlation in cold environments. The strongest positive PM₂.₅–O₃ correlation at high temperature, however, is mainly attributed to the promoting effect of high O₃ concentration and active photochemical activity on secondary particle formation in hot environments.

This paper revealed three underlying reasons for the PM₂.₅–O₃ correlations. It is noted that heterogeneous chemical reaction is an important way for PM₂.₅–O₃ interaction [17,59–62], which may also be a reason for the PM₂.₅–O₃ correlations. The formation of SOA with high O₃ concentration may contribute to positive correlations, because biogenic emission of VOCs is high under high temperature conditions in summer [20,25]. Furthermore, the variations in meteorological variables, through affecting transport and chemical processes of pollutants, may be important for daily variations in PM₂.₅ and O₃, and therefore, contribute to the PM₂.₅–O₃ correlations. Comprehensively understanding all these chemical and physical mechanisms needs more in-depth research through sensitivity experiments in future studies.

Supplementary Materials: The following are available online at http://www.mdpi.com/2073-4433/10/7/352/s1, Figure S1: Spatial-temporal distributions of surface temperature (°C). Each panel represents each month for year 2016.

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