Spatial and temporal distribution characteristics of ground-level nitrogen dioxide and ozone across China during 2015–2020

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Abstract

In recent years, the emissions control in nitrogen oxides (NOx) was conducted across China, but how the concentrations of NOx and its product ozone (O3) in the atmosphere varied in space and time remains uncertain. Here, the spatial and temporal distributions of nitrogen dioxide (NO2) and O3 in 348 cities of China based on the hourly concentrations data during 2015–2020 were investigated, and the relationships among NOx, O3 and meteorological and socioeconomic parameters were explored. It is shown that higher NOx and O3 concentrations were mainly distributed in North, East and Central China, which are economically developed and densely populated regions. The annual mean concentrations of NO2 increased from 2015 to 2017 but decreased from 2017 to 2020. The annual variations in O3 generally exhibited an upward trend in 2015–2019 but decreased by 5% from 2019 to 2020. About 74% and 78% of cities had a decline in NO2 and O3 in 2020, respectively, compared to 2019, due to the limits of the motorized transports and industrial production activities during COVID-19 lockdown. The monthly mean concentrations of NO2 showed an unusual decrease in February in all regions due to the reduced emissions during the Chinese Spring Festival holidays. Compared to 2019, the mean concentrations of NO2 in January, February and March, 2020 during COVID-19 lockdown decreased by 16%, 28% and 20%, respectively; O3 increased by 13% and 14% in January and February, respectively, but decreased by 2% in March, 2020. NO2 and O3 concentrations are likely associated with anthropogenic and natural emissions. In addition, meteorological parameters can affect NO2 and O3 concentrations by influencing the production process, the diffusion and local accumulation, and the regional circulations.

1. Introduction

Ground-level nitrogen dioxide (NO2) and ozone (O3) are major atmosphere pollutants that have negative impacts on human health (Li and Xin 2013, Chen et al 2017, 2018) and plants (Feng et al 2015, Tai and Val Martin 2017). For example, a large number of epidemiological studies have suggested that short- and long-term exposure to ambient NO2 and O3 have a variety of adverse health effects (Feng et al 2019b, Wang et al 2020), which induce and increase the risk of respiratory and cardiovascular diseases (Tao et al 2012), and irritate the eyes and skin (Liu et al 2018, Li et al 2020). In addition, previous studies reported that NO2 and O3 also have a significant contribution to changes in regional climate, e.g. temperature and precipitation (Feng et al 2019a). Moreover, NO2 and O3 were believed to have a crucial function in promoting the formation of nitrate (NO3−). NO3− is a secondary inorganic aerosol and its contribution to particulate matter (PM2.5) in the atmosphere can be up to 20%, which can reduce atmospheric visibility (Fu et al 2020, Zhao et al 2020).

In China, the National Ambient Air Quality Standards (GB 3095-2012) was issued by the Chinese Ministry of Environmental Protection in 2012 to control the emission amounts of pollutants, including six priority species NO2, O3, carbon monoxide (CO), sulfur dioxide (SO2), PM2.5 and PM10. In general, the NO2 concentrations have declined due
to the implementation of the Air Pollution Prevention and Control Action Plan from 2013 to 2017. While O\textsubscript{3} concentrations showed an increasing trend in urban and surrounding areas (Ma et al. 2016, Zeng et al. 2019).

Ground-level O\textsubscript{3} is a secondary atmospheric pollutant formed by photochemical reactions of its precursors (i.e. nitrogen oxides (NO\textsubscript{x} = NO + NO\textsubscript{2}), volatile organic compounds (VOCs) and CO) in the presence of sunlight. NO can be oxidized to NO\textsubscript{2}, which is a short-lived chemically active gas. The photolysis of NO\textsubscript{2} by sunlight can generate the highly active monatomic oxygen (O) (R1), then O combines with O\textsubscript{2} to form O\textsubscript{3} (R2) (Xiong and Du 2020). The generation of NO\textsubscript{2} can consume O\textsubscript{3} (R3) (He et al. 2018, Wang et al. 2019a). O\textsubscript{3} and NO\textsubscript{2} can react with each other to generate NO\textsubscript{3} radicals (R4).

\[
\text{NO}_2 + \text{hv} \rightarrow \text{NO} + \text{O}(^1\text{P}) \quad \text{(R1)}
\]

\[
\text{O}(^1\text{P}) + \text{O}_2 + \text{M} \rightarrow \text{O}_3 \quad \text{(R2)}
\]

\[
\text{NO} + \text{O}_3 \rightarrow \text{NO}_2 + \text{O}_2 \quad \text{(R3)}
\]

\[
\text{NO}_2 + \text{O}_3 \rightarrow \text{NO}_3 + \text{O}_2 \quad \text{(R4)}
\]

The formations of NO\textsubscript{2} and O\textsubscript{3} both have multiple pathways, so the relationship between O\textsubscript{3} and NO\textsubscript{2} is nonlinear. In addition, the NO\textsubscript{2} and O\textsubscript{3} abundances in the atmosphere are also affected by the meteorological conditions (Cao et al. 2012), local emissions, and long-distance transmission (Yan et al. 2021). A number of studies have shown that the O\textsubscript{3} formation largely depends on the photochemical regime and precursors emissions, i.e. whether O\textsubscript{3} production is VOC-limited or NO\textsubscript{x}-limited (Jin and Holloway 2015). And the O\textsubscript{3} formation sensitivity regimes are defined by the ratio of formaldehyde (HCHO) and NO\textsubscript{2}, with the ratios less than 1.0 and greater 2.0 indicating VOC-limited and NO\textsubscript{x}-limited regimes, respectively (Wang et al. 2021). A VOC-limited regime is usually found in urban areas in North and East China and VOC emission reductions can eliminate the local O\textsubscript{3} pollution (Yan et al. 2021). In suburban areas in Southwest and Northwest China, the O\textsubscript{3} formation sensitivity is NO\textsubscript{2}-limited and NO\textsubscript{x} emissions reduce ambient O\textsubscript{3} (Wang et al. 2021). NO\textsubscript{x} is emitted from anthropogenic combustion sources (i.e. industry, transportation, power plant and residential processes) and natural sources (i.e. lighting, soil and biomass burning). Emissions from power plants, transportation and industry are about 85% of the total NO\textsubscript{x} emissions over China. Soil NO\textsubscript{x} emissions are about 11%–20% of the anthropogenic sources (Anenberg et al. 2017, Zhao et al. 2020). Previous studies reported that soil NO\textsubscript{x} emissions via microbial processes have reached 20% and 3%–6% of the anthropogenic emissions in North and East China, respectively (Lin 2012, Lu et al. 2021). The emissions of NO\textsubscript{x} have decreased by 20% in China during 2013–2017 (Zheng et al. 2018, Li et al. 2019c). However, the VOCs emissions are estimated to have increased continuously due to large amounts of emissions from industries (solvent usage, industry, and petrochemical plant) and transportation (vehicular emission and vehicular fuel evaporation) (Zheng et al. 2018). Therefore, the NO\textsubscript{x}-VOC limitations of the O\textsubscript{3} formation regimes were complicated and changeable in different times and areas.

Previous investigations on spatial and temporal variations of NO\textsubscript{2} and O\textsubscript{3} in the atmosphere were carried out in China, and most of the observations were mainly via remote sensing or focus on a few specific regions in a short time scale (Ou et al. 2017, Yang et al. 2017, Wang et al. 2018). In recent years, especially after a new law on environmental prevention was implemented on 1 January 2015, which aims to improve the ecological and sustainable development, the emissions control in NO\textsubscript{x} was conducted across China, but how the concentrations of NO\textsubscript{2} and O\textsubscript{3} in the atmosphere varied in space and time remains uncertain. Therefore, the major objectives of this study were: (a) to obtain the NO\textsubscript{2} and O\textsubscript{3} concentrations data of 348 cities during 2015–2020, and to investigate the spatial and temporal (annual, seasonal, monthly and diurnal) variations in the NO\textsubscript{2} and O\textsubscript{3} concentrations, and (b) to study the potential effects of the socioeconomic and meteorological parameters on the NO\textsubscript{2} and O\textsubscript{3}.

2. Data and methods
2.1. Study regions
This study focuses on the 348 cities of the urban air quality monitoring stations over mainland China. According to China’s physical geographical features and socioeconomic factors, the 348 cities were classified into seven geographical regions: Northeast China, North China, Northwest China, Central China, East China, South China and Southwest China (figure 1).

2.2. Data sources
The China National Environmental Monitoring Center began to release hourly averages of six pollutants concentrations in 74 cities since 2013, and expanded to all of the prefecture-level cities since January, 2015. NO\textsubscript{2} and O\textsubscript{3} hourly concentrations data of 367 cities from 2015 to 2020 were collected from the China Ministry of Ecology and Environment on the website http://beijingair.sinaapp.com/. Following ‘technical regulation for ambient air quality assessment of China’ (on trial) (HJ 633-2013) issued by the Ministry of Environmental Protection of China,
among the datasets, months with minimum data of 27 days and years with at least 324 days were effective, and consequently, effective data of 348 cities were used for analysis. Here, the maximum daily 8 h average (MDA8) $O_3$ concentration in a day represents the daily $O_3$ level, and more details can be found in Fan et al (2020).

For investigation of the potential relationships between NO$_2$, $O_3$ and meteorological and socioeconomic parameters, we collected the meteorological data in 348 cities in 2020 from the China Meteorological Data Network (http://data.cma.cn). The meteorological data include the daily mean temperature, relative humidity, sunshine duration, air pressure, wind speed and daily precipitation. The socioeconomic data in 348 cities during 2015–2018 are from the China City Statistical Yearbook (2015–2018), including the ratios of secondary industry, per capita gross domestic product (GDP), population and the number of cars.

### 2.3. Data analysis methods

The spatial and temporal (annual, seasonal, monthly) variations in NO$_2$ are analyzed by calculating the average of the hourly NO$_2$ concentrations. The spatial and annual $O_3$ variations calculated are from the 90th percentile of MDA8-$O_3$. Monthly and seasonal variations in $O_3$ are analyzed by calculating the average of MDA8-$O_3$. Diurnal variations in $O_3$ and NO$_2$ are analyzed by calculating the hourly $O_3$ and NO$_2$ concentrations. The regional averages represent mean values calculated from all cities in that particular region.

Figure 1. The distribution of seven geographical regions in China.

To characterize the temporal and spatial variations in ground-level NO$_2$ and $O_3$ concentrations, ArcGIS10.2 tools are used to visualize the variations. Correlation analysis of NO$_2$, $O_3$, and meteorological and socioeconomic parameters are conducted with the aid of SPSS Statistics 21. Correlation analysis method is the Pearson’s correlation analysis ($r$). Pearson’s correlation coefficient can evaluate the strength of a linear relationship between two variables, which is defined as:

$$r = \frac{\sum_{i=1}^{n} [(x_i - \bar{x}) \cdot (y_i - \bar{y})]}{\sqrt{\sum_{i=1}^{n} (x_i - \bar{x})^2} \cdot \sqrt{\sum_{i=1}^{n} (y_i - \bar{y})^2}}$$

where $\bar{x}$ and $\bar{y}$ are the means of two variables and $n$ is the sample number. $r$ value ranges from $-1$ to $+1$.

### 3. Results and discussion

#### 3.1. Spatial distribution of NO$_2$ and $O_3$

NO$_2$ and $O_3$ annual mean concentrations both had clear spatial variations over China during 2015–2020 (figure 2). The regions with higher NO$_2$ concentrations were mainly concentrated in North, East and Central China, which are economically developed and densely populated regions. These regions usually have energy-intensive heavy industries, large amounts of cars and coal-fired power plants, which emitted large amounts of NO$_x$ (Jiang et al 2020), and consequently NO$_2$ concentrations were higher. But most cities in South and Southwest China usually have small scales of industries, and thus NO$_2$ concentrations are expected to be lower.
Similar to NO$_2$, high O$_3$ concentrations were mainly concentrated in North, East and Central China. The clearly higher concentrations of O$_3$ in some cities may be attributed to the elevated concentrations of its precursors (NO$_x$, CO and VOCs), which are mainly emitted from the vehicle and industrial emissions, and biomass burning (Cheng et al 2019, Tang et al 2020).

3.2. Temporal variation of NO$_2$ and O$_3$

3.2.1. Diurnal and nocturnal variations in NO$_2$ and O$_3$

The average diurnal and nocturnal profiles of NO$_2$ and O$_3$ in different years showed similar trends in all regions (figures 3 and 4). The diurnal and nocturnal variations of NO$_2$ were pronounced with a bimodal pattern, and the peaks appeared mostly in the periods of 8:00–9:00 and 22:00–23:00, with a minimum at approximately afternoon (figure 3). The NO$_2$ concentrations maximum during 8:00–9:00 is possibly due to a low atmospheric boundary layer and higher NO$_x$ emissions during the traffic rush hours (Fan et al 2020). In general, NO$_2$ concentrations decrease from the morning to the afternoon. During this period, a boundary layer usually begins to form and its height increases after sunrise, which helps to dilute pollutants (Kalsoom et al 2021). In addition, in the presence of sunlight, the strong solar radiation and high temperature are conducive to the photochemical reactions and would consume large amounts of NO$_2$ to produce O$_3$ (R1 and R2) (Fang et al 2019). Then the atmospheric boundary layer height and photochemical reactions begin to decrease, and the NO$_2$ concentrations again increase and reach the peak values at 22:00–23:00 (Zhang et al 2019b).

The diurnal and nocturnal variations of O$_3$ concentrations were quite different from that of NO$_2$, which displayed a unimodal pattern (figure 4). O$_3$ concentrations were relatively low in the morning around 6:00–8:00 (average = 38 µg m$^{-3}$) due to the decrease or absence of photochemical reaction of R1 (Zhang et al 2019a) and reached the highest values between 15:00 and 16:00 (93 µg m$^{-3}$) (Fang et al 2019, Rahman et al 2019). After 16:00, the O$_3$ concentrations gradually decreased until 6:00–8:00 in the next day.

3.2.2. Monthly variation in NO$_2$ and O$_3$

From January to December, the monthly mean concentrations of NO$_2$ showed clear concave profiles (figure 5). The NO$_2$ concentrations range from 20 µg m$^{-3}$ (July) to 41 µg m$^{-3}$ (November) during 2015–2020. NO$_2$ concentrations decreased from January to July, and then increased from July to December, reaching the highest values in November–January. It is noted that NO$_2$ concentrations showed an unusual decrease in February in all regions, which is likely associated with the Chinese Spring Festival holidays which is usually around February. During the Spring Festival, the traffic flow drops and the industrial plants are almost entirely shut down, which is likely to cause the emissions of pollutants to reduce remarkably (Wang et al 2017).

In addition, it is noted that NO$_2$ levels were lower in 2020 than in the antecedent years in most cities. In general, the average NO$_2$ concentrations exhibited a decrease for seven regions in all months in 2020, compared with the five-year (2015–2019) averages. The average NO$_2$ concentrations in January, February and March, 2020 decreased by 16%, 28% and 20% for all cities, respectively, compared to those in 2019 (figure 3). Since December 2019, the COVID-19 (coronavirus disease 2019) firstly broke out in Wuhan and has been spreading in Chinese mainland (Tian et al 2020). The China central government launched lockdown measures in Wuhan in January, 2020 and then began initiating the first-level response to a major public health emergency in other cities (Chen et al 2020b). These measures have limited the motorized transports and slowed down China’s industrial production activities and economic growth significantly, and consequently emissions of pollutants reduced remarkably (Pei et al 2020, Sicard et al 2020, Chen et al 2020a). In April 2020, all the cities in China terminated their public health emergency first-level response. Then, NO$_2$ concentrations increased to
a similar level in April 2020 as in previous years due to rebounded economy and increased energy consumption.

Different from NO₂, O₃ concentrations showed a convex shape profile and exhibited varied patterns in different regions from January to December (figure 6), which agrees with previous studies (Li et al 2019a, Wang et al 2019b). O₃ concentrations range from 49 µg m⁻³ (December) to 117 µg m⁻³ (June) during 2015–2020. The monthly variation trend of O₃ concentrations showed a distinct inverted V-shaped curve in Northeast, Northwest and North China (figures 6(e)–(g)). The O₃ concentrations increased from January to June, reaching the peaks around June, and then decreased from June to December. However, the monthly mean concentrations of O₃ showed an M-shaped curve in South, Southwest, Central and East China (figures 6(a)–(c)), which could be associated with the summer monsoon. Summer monsoon mainly occurs in June–July and could bring large clouds and precipitation, which can inhibit photochemical production, transports and diffusion of O₃ (Chen et al 2020c). Different from other regions, in Southwest China, a combination of stronger ultraviolet radiation and temperature favoring the formation of the O₃ and strong stratospheric O₃ intrusions possibly results in the O₃ peaks during April–May (Liu et al 2019). In South China, the increased photochemical production associated with the weather conditions (e.g. strong solar radiation, prevailing northerly and northeasterly winds) and the increasing anthropogenic emissions of its precursor VOCs in September–October are also conducive to the formation of the O₃ (Huang et al 2013), and consequently, the maxima are generally present in September–October.

Over 2015–2019, O₃ concentrations in most months exhibited an increasing trend, with the largest

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**Figure 3.** Diurnal and nocturnal variations in NO₂ in different regions during 2015–2020, with diurnal and nocturnal profiles from averages over 365 days in a year.
Figure 4. Diurnal and nocturnal variations in $O_3$ in different regions during 2015–2020, with diurnal and nocturnal profiles from averages over 365 days in a year.

Increases in April–September when photochemical reactions are strong (figure 6). The photochemical regime of $O_3$ is VOC-limited in most cities in winter due to the relative lack of HOx radicals. And the NO2 photolysis reduces due to the low ultraviolet intensity during winter (Wang et al. 2021). Therefore, the $O_3$ concentrations could decrease due to the reduction in local VOCs and NOx emissions during the COVID-19 lockdown. However, compared with 2019, the average $O_3$ increased by 13% and 14% for all cities (32% and 55% in Wuhan) in January and February 2020, respectively. This may be related to that the NOx emissions reduction is greater than that of the VOCs emissions, and thus leads to an increase in the $O_3$ concentrations (Sicard et al. 2020). A decrease in NOx emissions can decrease the concentrations of PM2.5, possibly reducing the reactive uptake of HOx radicals which can react with NO to form NO2 and subsequently influence the production of $O_3$ in the atmosphere (Li et al. 2019b, Chu et al. 2021). In addition, the less NO to react with $O_3$ would also cause an increase in $O_3$ concentrations (Wang et al. 2013, Wu and Xie 2017).

3.2.3. Seasonal variation in NO2 and O3
The highest concentrations of NO2 mainly occurred in winter (December–February), with a mean value of $36 \pm 12 \mu g m^{-3}$, followed by autumn ($31 \pm 11 \mu g m^{-3}$; September–November) and spring ($28 \pm 9 \mu g m^{-3}$; March–May), and the lowest value is present in summer ($20 \pm 7 \mu g m^{-3}$; June–August) (figure 7). Some recent investigations suggested that soil emissions are important sources of NOx in the atmosphere, which are dependent on a variety of environmental conditions (i.e. soil temperature, moisture, nitrogen availability and PH).
Figure 5. Monthly variation in the NO\textsubscript{2} in seven geographical regions during 2015–2020. Also shown is the five-year averages during 2015–2019.

(Oikawa et al 2015, Molina-Herrera et al 2017), with high emissions in summer and low emissions in winter (Romer et al 2018). If soil emissions are the main sources of NO\textsubscript{2}, the higher NO\textsubscript{2} would be expected in summer, in contradiction to the observations (figure 7). It is suggested that soil emissions are not an important source to NO\textsubscript{2} emissions.

Different from NO\textsubscript{2}, in general, the highest O\textsubscript{3} concentrations appeared in summer (156 ± 34 µg m\textsuperscript{-3}), followed by spring (146 ± 23 µg m\textsuperscript{-3}) and autumn (131 ± 28 µg m\textsuperscript{-3}), with the lowest in winter (92 ± 12 µg m\textsuperscript{-3}) (figure 8). It is noted that the seasonal patterns of O\textsubscript{3} in different cities are varied, i.e. more than 64% of cities in Northeast, North, East, Northwest, Central and Southwest China have the highest O\textsubscript{3} concentrations in summer, while 18% of cities in Northeast and Southwest China are in spring. In addition, the maxima of more than 18% of cities in South, Central and East China are present in autumn. This may be associated with that the changes in meteorological parameters and precursors pollutant concentrations can influence the photochemical reactions, decomposition and dispersion of O\textsubscript{3} (Cheng et al 2019, Chen et al 2020d).

3.2.4. Annual variation in NO\textsubscript{2} and O\textsubscript{3}

In general, the annual mean of NO\textsubscript{2} increased from 2015 to 2017 but decreased during 2017–2020 (figure 9(a)). Compared to 2017, the average NO\textsubscript{2} concentrations decreased by 8%, 11% and 17% in 2018, 2019 and 2020, respectively. And the average NO\textsubscript{2} concentrations decreased by 7% in 2020, compared with 2019. Compared with 2015, the annual mean concentrations of NO\textsubscript{2} in 63% of cities decreased in 2019 (figure 10(a)). It is noted that NO\textsubscript{2} concentrations had clear decreasing trends for all regions, and 74% of cities had a decline in NO\textsubscript{2} in 2020, compared with 2019 (figure 10(c)). The decrease of NO\textsubscript{2} concentrations is likely associated with emission control measures and active clean air policies in China. Fan et al (2020) also reported that the emissions of NO\textsubscript{x} have been reduced in seven regions of China during 2014–2017, which is the major contributing factor for the reduction of atmospheric NO\textsubscript{2}.
In 2015–2019, the annual variation in \(O_3\) generally exhibited an upward trend (figure 9(b)). Compared with that in 2015, \(O_3\) concentrations increased by 9%, and 68% of cities showed an increase in \(O_3\) in 2019, with the largest increasing rate in North China (21%) (figure 10(b)). The increase of \(O_3\) could be associated with the decrease in NO\(_x\) emissions in the VOC-limited (or NO\(_x\)-saturated) regime. For example, 42% of cities showed an increase in \(O_3\) with decreasing NO\(_2\) concentrations, which were mainly concentrated in North, East and Central China. However, \(O_3\) concentrations show similar trends with that of NO\(_2\) in some cities. Jin and Holloway (2015) and Wang et al. (2021) reported that the VOC-limited regimes mainly appear in North, central and East China, and the NO\(_x\)-limited regimes dominate the other cities. In addition, the anthropogenic VOC emissions showed a large increase trend over 2005–2019 (Jin and Holloway 2015, Wang et al. 2021). Therefore, \(O_3\) concentrations would increase with decreasing NO\(_x\) emissions. In the future, the simultaneous emissions reduction of VOC and NO\(_x\) could be more effective in reducing \(O_3\) concentrations. In comparison with 2019 (149 ± 26 \(\mu g \text{ m}^{-3}\)), the \(O_3\) levels decreased in 2020, when the annual mean of (140 ± 23 \(\mu g \text{ m}^{-3}\)) is comparable to that in 2016 (140 ± 25 \(\mu g \text{ m}^{-3}\)). It is noted that 78% of cities had a decline in \(O_3\) in 2020, compared to 2019 (figure 10(d)). The decrease of \(O_3\) could be associated with the meteorological conditions and the decrease in NO\(_x\) emissions (see section 3.4).

3.3. The relationship between NO\(_2\), \(O_3\) and socioeconomic parameters
Significant positive correlations were found between the NO\(_2\), \(O_3\) and socioeconomic parameters in different regions during 2015–2018, especially between NO\(_2\) and socioeconomic parameters (table 1). The correlation coefficients between population, the number of cars and NO\(_2\) were positive in seven regions \((p < 0.05; \text{table } 1)\), indicating that NO\(_2\) concentrations are closely associated with the emissions, possibly from the industrial activities and vehicle emissions (Wu et al. 2016, Yang et al. 2019b). Previous studies reported that a substantial increase in total vehicle NO\(_x\) emissions in China, and this source contributed approximately 12%–36% of the total NO\(_x\) (Wu et al. 2016). In addition, NO\(_2\) concentrations
were positively correlated with per capita GDP in most regions (table 1). It is reported that the relationship between per capita GDP and atmospheric pollutants exhibited an inverted U-shaped environmental Kuznets curve (EKC) (Zhou et al 2017). That is, when economic development reaches a high level, the governments began to pay attention to environmental protection by transforming industrial and energy structures, increasing environmental protection budgets and enacting local laws and regulations,
Figure 9. Variations of annual average concentrations of (a) NO\textsubscript{2} and (b) O\textsubscript{3} in 348 cities in China.

Figure 10. The percent change of NO\textsubscript{2} (a) and O\textsubscript{3} (b) in 2019, compared to 2015 (percent change = (\(C_{2019} - C_{2015}\))/\(C_{2015}\)), where \(C\) is the annual mean concentrations of NO\textsubscript{2} or O\textsubscript{3}, and the percent change of NO\textsubscript{2} (c) and O\textsubscript{3} (d) in 2020, compared to 2019 (percent change = (\(C_{2020} - C_{2019}\))/\(C_{2019}\)).

Table 1. The Pearson's correlation coefficients between NO\textsubscript{2} (O\textsubscript{3}) and socioeconomic parameters during 2015–2018.

| Regions          | The ratios of secondary industry | Per capita GDP | Cars | Population |
|------------------|----------------------------------|----------------|------|------------|
| Northwest China  | \(-0.065 (0.342^a)\)            | 0.242 (0.194\(^b\)) | 0.570 (0.084) | 0.523 (0.253\(^a\)) |
| South China      | 0.077 (0.257\(^a\))             | 0.486 (0.283\(^a\)) | 0.531 (0.314\(^a\)) | 0.563 (0.213\(^a\)) |
| Central China    | 0.183 (0.012)                   | 0.158 (0.135)      | 0.421 (0.161\(^a\)) | 0.388 (0.148) |
| Southwest China  | 0.313 (0.206\(^a\))             | 0.283 (0.076)      | 0.570 (0.274\(^a\)) | 0.531 (0.275\(^a\)) |
| North China      | 0.079 (0.065)                   | 0.029 (0.082)      | 0.236 (0.203\(^a\)) | 0.358 (0.248\(^a\)) |
| East China       | \(-0.072 (0.081)\)              | \(-0.063 (0.061)\) | 0.327 (0.169\(^a\)) | 0.370 (0.262\(^a\)) |
| Northeast China  | 0.424 (0.432\(^a\))            | 0.414 (0.397\(^a\)) | 0.581 (0.188\(^b\)) | 0.573 (0.182\(^b\)) |

\(^a\) Significant at \(p < 0.01\).
\(^b\) Significant at \(p < 0.05\). The numbers in the parenthesis are for the Pearson's correlation coefficients between O\textsubscript{3} and socioeconomic parameters.
and thus pollutants emissions would reduce. But in parts of China, the degree of economic development did not reach a high level and remains on the left side of the turning point of EKC (Ding et al. 2019), that is, economic growth would bring more air pollution.

Similar to NO$_2$, the number of cars and population were also positively correlated with O$_3$ concentrations in most regions (table 1). The atmospheric pollutants emitted by vehicular exhaust include NO$_x$, VOCs, hydrocarbon (HC) and CO, which are the precursors of O$_3$ (Johnson 2017, Yang et al. 2019b). For example, Lyu et al. (2016) found that vehicular emissions were the main contributors to VOCs in Wuhan (27.8%), and the fraction O$_3$ formation via the VOCs channel accounts for as high as 23.4% of the total atmospheric O$_3$ budget. In addition, high O$_3$ precursors emissions also were mainly concentrated over densely populated areas due to the intensive production activities, and thus the more population could result in the elevated concentrations of O$_3$ (Meng and Zhou 2020). Therefore, large amounts of precursors of O$_3$ emitted into the atmosphere through the energy consumption, burning fossil fuel, and vehicle exhaust emissions (Zheng et al. 2018), could be responsible for the correlation observed between O$_3$ concentrations and population and cars.

3.4. The relationships between NO$_2$, O$_3$ and meteorological parameters

Meteorological parameters can affect NO$_2$ and O$_3$ concentrations by influencing the rate of photochemical reaction, the diffusion and local accumulation and the transport between regions (Elminir 2005, Ramsey et al. 2014). Here, we calculated the Pearson’s correlation coefficients between daily mean concentrations of NO$_2$, O$_3$ and meteorological parameters in 348 cities in 2020 (figures 11 and 12). The results show that meteorological influences on the NO$_2$ and O$_3$ trend differed by regions.

Figure 11. Pearson’s correlation coefficients between NO$_2$ and meteorological parameters in 2020 (n = 365, open circles indicate $p > 0.05$, and thus the Pearson’s correlation coefficients are not presented, and the closed circles indicate correlation is significant at $p < 0.05$, with colors representing the correlation coefficients).
NO$_2$ concentrations were negatively correlated with relative humidity in most cities, and this correlation was much stronger in Central and Southwest China (figure 11(a)). An increase in relative humidity is often accompanied by rainfall and increases in cloud cover and wind speed (Chen et al 2020d), which could increase wet deposition of NO$_2$ and consequently could lower the concentrations of NO$_2$ in the atmosphere. In this case, it is expected that precipitation also showed a negative correlation with NO$_2$ concentrations, generally in line with the observations (figure 11(b)). In addition, it is reported that the reaction of NO$_2$ with OH decreased at a lower relative humidity (Elminir 2005), and thus NO$_2$ concentrations would increase at a lower relative humidity. However, a positive correlation between NO$_2$ and relative humidity was observed in Northwest China, and this may be associated with that higher relative humidity could increase atmospheric stability and the formation of temperature inversion, which suppress the vertical diffusion of NO$_2$ (Yang et al 2019a, Zhou et al 2020).

NO$_2$ concentrations were negatively correlated with temperature (figure 11(c)). It is reported that the photochemical reaction of NO$_2$ (R1) and the vertical dispersion would increase under the higher temperature (Yang et al 2019a). Thus, lower NO$_2$ concentrations were usually present at higher temperature. In addition, the association between NO$_2$ concentrations and sunshine duration was found to be weak or insignificant in most cities (figure 11(d)).

In general, NO$_2$ concentrations were positively correlated with atmospheric pressure (figure 11(e)). A high atmospheric pressure is usually associated with the downward flow of the center area, so it is not conducive to the dilution and diffusion of NO$_2$. Higher wind speed is conducive to the atmospheric mixing, transport and dispersion, and thus the NO$_2$ would be expected to be dilute, likely supported by the observations (figure 11(f)).
In general, O$_3$ concentrations were also negatively correlated with relative humidity (figure 12(a)). These correlations became stronger in Southwest and South China. The higher relative humidity could reduce the ultraviolet radiation resulting in the decrease in photochemical O$_3$ production (Zhou et al 2020). However, the relationship between O$_3$ concentrations and precipitation was weak or insignificant (figure 12(b)), suggesting that O$_3$ is not dominated by precipitation.

O$_3$ concentrations were positively correlated with temperature and sunshine duration (figures 12(c) and (d)). Effects of temperature on O$_3$ are higher in Northwest and North China. Increasing temperature directly promotes the formation of O$_3$ by accelerating the rate of photochemical reactions (Li et al 2017). Therefore, we can find that higher O$_3$ concentrations in spring or summer and the lowest O$_3$ concentrations in winter (figure 8). In addition, temperature changes can indirectly affect the formation of O$_3$ by causing changes in biological emissions (e.g. VOCs, the O$_3$ precursors) (Liu and Wang 2020), thus influencing O$_3$ levels.

Different from NO$_2$, O$_3$ concentrations were negatively correlated with pressure (figure 12(e)), suggesting that the O$_3$ is unlikely controlled by atmospheric diffusion process. The high-pressure synoptic system is usually associated with low temperature and high wind speed and humidity (Fang et al 2019), which inhibits the formation and accumulation of O$_3$. For the secondary pollutant O$_3$, the dilution of aerosol concentrations by wind could increase surface ultraviolet radiation and strengthen O$_3$ productivity (Liu et al 2020), possibly resulting in an indirect positive correlation between wind speed and O$_3$ (figure 12(f)).

4. Conclusions

We investigated the spatial and temporal variations in NO$_2$ and O$_3$ in 348 cities of China during 2015–2020. The regions with the higher NO$_2$ and O$_3$ concentrations were mainly distributed in North, East and Central China, which are economically developed and densely populated regions. The diurnal and nocturnal variation of NO$_2$ were pronounced with a bimodal pattern, where the peaks appeared mostly in the periods of 8:00–9:00 and 22:00–23:00 and a minimum was at approximately afternoon. The diurnal and nocturnal variation of O$_3$ concentrations displayed a unimodal pattern and reached the highest values between 15:00 and 16:00. The monthly mean concentrations of NO$_2$ showed clear concave profiles and had an unusual decrease in February in all regions due to the reduced emissions during the Chinese Spring Festival holidays. The monthly mean concentrations of O$_3$ presented an M-shaped curve in South, Southwest, Central and East China, which were strongly influenced by the summer monsoon.

Compared to 2019, the mean concentrations of NO$_2$ in January, February and March, 2020 decreased by 16%, 28% and 20% in all cities, respectively, due to the limited of motorized transports and industrial production activities during COVID-19 lockdown. However, compared to 2019, the mean concentrations of O$_3$ increased by 13% and 14% in all cities in January, and February, 2020, respectively, due to a decrease in NO$_2$ emissions. The annual mean concentrations of NO$_2$ increased from 2015 to 2017 but decreased from 2017 to 2020. The annual variation in O$_3$ generally exhibited an upward trend in 2015–2019 but decreased by 5% from 2019 to 2020. Compared with 2019, 74% and 78% of cities had a decline in NO$_2$ and O$_3$ in 2020, respectively.

NO$_2$ and O$_3$ concentrations are likely associated with anthropogenic and natural emissions. In addition, meteorological parameters can affect NO$_2$ and O$_3$ concentrations by influencing the production process, the diffusion and local accumulation and the regional circulations. It is acknowledged that the interpretation of spatial and temporal variations in NO$_2$ and O$_3$ based on the correlation analysis remains uncertain, and further investigations are needed to characterize the atmospheric chemical formation mechanism of NO$_2$ and O$_3$.

Data availability statement

The data that support the findings of this study are available upon reasonable request from the authors.

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