Feature analysis on air quality in the main urban area of Nanchong City in 2015–2018

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Abstract
This study evaluates the air quality in Nanchong City in 2015–2018 based on automatic monitoring data and meteorological data in the main urban area. Results show that overall air quality in the main urban area of Nanchong was standard and improved from 2015 to 2018. SO2, NO2, and CO had slight influences on air quality in the study area, whereas excessive annual average PM2.5 and increasing O3 concentration challenged the air quality. The monthly average mass concentrations of particulate matters (PM2.5 and PM10), NO2, and CO generally presented a “U-shaped” distribution pattern while O3 showed the opposite. The diurnal variation of PM, NO2, and CO has two peaks related to the morning and evening rush hours. Vehicle exhaust is the main source of local pollution. Over-standard PM2.5 can significantly inhibit O3 production while O3 can easily promote the secondary generation of PM2.5 due to its strong oxidation. PM2.5 emission should be controlled strictly in winter, while in summer, the sources of O3 should be controlled vigorously. Air pollution is comprehensive and complicated and is influenced by various factors, mainly meteorological and human factors. Measures such as artificial rainfall should be included at the appropriate time to cope with adverse meteorological conditions when heavy pollution occurs in winter.

Keywords: Air quality, Meteorological factor, Nanchong, O3, PM2.5
1. Introduction

Air pollution in China has intensified along with the progresses in industrialization and urbanization [1]. In the last 30 years, the main air pollutants in China have undergone several stages, from total suspended particulates, inhalable particles (PM$_{10}$), and sulfur dioxide (SO$_2$) to fine particulate matters (PM$_{2.5}$) and ozone (O$_3$), because of increased production capacity, energy restructuring, and a sharp increase in car ownership [2–4]. Pollution types evolved from cumulative over-standard single pollutants into composite pollution caused by the coexistence of several pollutants. At present, air pollution in most Chinese cities is identified as composite pollution [5–7], and transregional large-scale environmental problems have formed [8, 9]. Anthropogenic source is the primary one between two major sources of air pollutants [9]. Air pollution in most cities in China is the same as in Japan, Korea, and many European and American countries [10, 11]. It is mainly influenced by production and the living activities of human beings, such as combustion of fossil fuel, combustion of biomass, industrial production and emission, and vehicle exhaust [12]. There are complicated conversion relations among pollutants that have entered the atmospheric environment and between pollutants and original air components [5]. For example, SO$_2$ and NO$_2$ can generate secondary particulates through homogenous and heterogeneous reactions [13], which play an important role in regional air quality and global climate changes [14]. Ozone precursors such as NO$_x$ and volatile organic compounds (VOCs) can produce near-surface O$_3$ through photochemical reactions [15–17]. In addition, ozone is closely related to the formation of PAHs, and PAHs are seriously harmful to human body [18, 19]. Pollutants that enter the air not only cause serious damage to the environment and the physical health of humans but may also jeopardize sustainable economic
and social development [20–22]. A study [23] has pointed out the existence of an inverted U-shaped curve relation between economic development and pollution. In other words, air quality declines with the increase in per capita income.

Given the advances in air quality monitoring methods and the increasing efforts in air pollution study and control, air quality problems in China have generally improved significantly. Most existing research on air quality emphasizes heavily polluted big cities (e.g., Beijing-Tianjin-Hebei, Yangtze River Delta, Pearl River Delta, and Sichuan Basin) [24–29] or economically developed cities. However, there are relatively fewer studies concerning air quality in small and middle cities. China also has an extensive territory with different landforms and levels of economic development modes. Hence, measures and methods to control air pollution vary for different regions. Air pollution is generally related to climate [30]. Many studies have demonstrated that meteorological factors, such as air temperature, rainfall, and wind speed, are important influencing factors of air pollutant concentrations [13, 31, 32]. In particular, migration, transformation, dilution, and diffusion of pollutants in air are mainly determined by meteorological factors when the pollutant source is relatively stable [17, 33]. Temporal and spatial variations of air pollutants are closely related to emission source, geographic features, and climatic factors [13].

Nanchong City is located in the northeast region of Sichuan Basin. Its main urban area is at the bottom and low-lying. As conditions for the diffusion of pollutants in the city are poor, pollutants accumulate easily [34]. Having suffered great damages due to acid rain, Nanchong City implemented the coal-to-gas project in its main urban area in 2000 [35], and it has had no acid rains since 2015 [36]. Nevertheless, PM$_{2.5}$ and O$_3$ pollutions are still prominent, the same as
in other Chinese cities [5, 37]. A great agricultural city, Nanchong is characteristic of cities with underdeveloped industries and a big population (the population in the main urban area reached 1.37 million in the end of 2018). The activities of residents (e.g., production and commuting) and the pollutants produced by biomass combustion in suburbs considerably influence the air quality in urban areas [38]. Although some studies on air pollution in Nanchong City (mainly short-term air quality analyses) have been reported, no long-term and systematic analysis of air quality in the main urban area of the city has been carried out. In the present study, the variation trend of air quality in the main urban area of Nanchong City in recent years was analyzed systematically using automatic monitoring data in 2015–2018. In addition, monthly and diurnal variations of air pollutants and their relations with PM$_{2.5}$ and O$_3$ were discussed by combining them with meteorological data. Causes of haze pollution and intensifying O$_3$ pollution were likewise explored to provide references for air pollution control in Nanchong City.

2. Study Area and Data Source

2.1. Study Area

Nanchong City (30°35′–31°51′ N, 105°27′–106°58′ E, 256–889 masl) is located in the northeast of Sichuan Basin and the midstream of Jialing River. It is the city with the second biggest population in Sichuan Province. It belongs to the mid-subtropical mild monsoon climate zone, which has cloudy and misty weather accompanied by low wind speed and quiet winds in a year, especially in winter [17]. The main urban area of Nanchong City is in the south, which includes the districts of Shunqing, Gaoping, and Jialing. It is located on the valley terrace and has low-
lying terrain, with an elevation of only about 300 m. It is high in the northwest and low in the southeast. The study area is shown in Fig. 1.

2.2. Data Source

Air quality data in this study were collected from automatic monitoring data in the Environmental Monitoring Center of Nanchong City from January 1, 2015 to December 31, 2018, including standard air pollutants (PM$_{2.5}$, PM$_{10}$, SO$_2$, CO, NO$_2$, and O$_3$) and air quality index (AQI). Meteorological data were collected from the website (https://rp5.ru/), including daily data of temperature (T), air pressure (AP), relative humidity (RH), wind speed (WS), precipitation (P), and horizontal visibility (HV). According to the meteorological division method of China, one year is divided into spring (March–May), summer (June–August), autumn (September–November), and winter (December–February the next year).

AQI is calculated as follows:

$$\text{AQI} = \max \{\text{IAQI}_1, \text{IAQI}_2, \text{IAQI}_3, \ldots, \text{IAQI}_n\}$$

where IAQI is the individual air quality index, and n is the pollutant project.

AQI is a dimensionless index that provides a quantitative description of air quality. The higher the numerical value of AQI, the higher the degree of pollution [17]. Air quality level is divided into six levels: I (0–50), II (51–100), III (101–150), IV (151–200), V (201–300), and VI (>300). These six levels correspond respectively to Excellent, Good, Mild pollution, Moderate pollution, Heavy pollution, and Serious pollution. Daily AQI reaching the Excellent or Good level is viewed as meeting the standard.
2.3. Research Method

2.3.1. Effects of PM$_{2.5}$ on O$_3$

According to the grading standards of PM$_{2.5}$ concentration in China [39], PM$_{2.5}$ concentration is divided into three levels: $< 35 \, \mu g/m^3$, $35-75 \, \mu g/m^3$, and $> 75 \, \mu g/m^3$. These three levels represent different air quality grades: Excellent, Good, and Polluted. The O$_3$ concentration at the current hour minus the O$_3$ concentration at the previous hour is the hourly variation rate of O$_3$. Data of O$_3$ were grouped according to PM$_{2.5}$ concentration at the same time to further investigate the hourly variation intensity of O$_3$ when PM$_{2.5}$ concentration varies.

2.3.2. Effects of O$_3$ on PM$_{2.5}$

In this study, the effects of O$_3$ on PM$_{2.5}$ were analyzed with reference to the method of Chang et al. [40] based on the percentage of secondary particulates under different O$_3$ concentrations. According to the grading standards of O$_3$ in China, the data of O$_3$ were divided into four levels: O$_3$ $<$ 100 $\mu g/m^3$, 100–160 $\mu g/m^3$, 160–200 $\mu g/m^3$, and $> 200 \, \mu g/m^3$. The mass concentration of secondary particulates is calculated as follows:

$$PM_{2.5S,i} = PM_{2.5T,i} - CO_{T,i} \times (PM_{2.5}/CO)_L$$

where $i$ is the interval of O$_3$ concentration; $PM_{2.5T,i}$ represents the PM$_{2.5}$ concentration when the interval of O$_3$ concentration is $i$; $PM_{2.5S,i}$ denotes the secondary PM$_{2.5}$ concentration when the interval of O$_3$ concentration is $i$; $CO_{T,i}$ refers to the CO concentration when the interval of O$_3$ concentration is $i$; and $(PM_{2.5}/CO)_L$ represents the value of PM$_{2.5}$/CO when O$_3$ $< 100 \, \mu g/m^3$.

2.4. Statistical Analysis
The statistical analysis was conducted using the SPSS 19.0 and Excel. Specifically, relationships between air pollutants and meteorological parameters were tested using the Spearman correlation. Kruskal-Wallis test was used to investigate the differences of annual pollutants concentrations from 2015 to 2018. \( P < 0.05 \) was considered to be of statistical significance.

3. Results and Discussion

3.1. Air Quality

Fig. 2 shows the mean AQI in the main urban area of Nanchong City in 2015–2018 was 68.52 and decreased year by year. The 75th percentile of the AQI was kept lower than 100 (Ambient air quality up to standard) for three successive years (2016–2018), and only the 95th percentile in 2015 was higher than 150 (Moderate pollution). This result reflects the significant achievements of air pollution control in recent years, as manifested by the improving air quality year by year.

When the analysis of annual average concentrations of six elements of ambient air quality in Nanchong City in 2015–2018 (Table S1) is combined with the Ambient Air Quality Standard (GB3095-2012) [39], it can be concluded that PM is the major over-standard pollutant in the study area. Specifically, \( \text{PM}_{2.5} \) exceeded the national Grade II standard of annual average concentration (35 \( \mu \text{g/m}^3 \)) for four years successively [39]. However, \( \text{PM}_{10} \) concentration dropped dramatically after 2016 and met the national Grade II standard of annual average concentration (70 \( \mu \text{g/m}^3 \)) after 2017 [39]. The concentrations of other gaseous pollutants were generally low and presented no over-standard phenomenon. The annual average concentrations of \( \text{NO}_2 \) and \( \text{O}_3 \) increased continuously. In particular, the annual average concentration of \( \text{O}_3 \) increased year by year, and the increasing amplitude reached the significant level (Kruskal-Wallis test, \( p < 0.01 \)).
The average $O_3$ concentration in 2018 increased 0.75 times compared to that in 2015 and reached 88.09 μg/m$^3$. This finding is consistent with the increasingly prominent $O_3$ pollution in other cities in China [41, 42].

Zhong et al. [43] pointed out that the rate of standard ambient air quality (percentage of Excellent and Good levels of ambient air quality) in the main urban area of Nanchong City in 2014 was only 66.80%, which was significantly lower than that during 2009–2013. This outcome was mainly due to the new Ambient Air Quality Standard (GB3095-2012) implemented in the main urban area of Nanchong City in 2014 and the increase in the main pollutants considered to judge ambient air quality from three items ($SO_2$, $NO_2$, and $PM_{10}$) to six ($SO_2$, $NO_2$, CO, $O_3$, $PM_{2.5}$, and $PM_{10}$) [39]. The judgment standards were increased as well, leading to a sharp rise in the number of over-standard days and a dramatic reduction in the percentage of Excellent and Good levels of ambient air quality in 2014. Similar phenomena were observed in big cities such as Beijing–Tianjin–Hebei, Yangtze River Delta, Pearl River Delta, and so on [29]. The number of days that meet the ambient air quality standard in Nanchong City has increased year by year since 2015 (Table S2). Specifically, the number of days in 2018 was 26 days higher compared to that in 2015, and the control rate reached as high as 87.12%. Fig. 3(a) illustrates that the overall percentage of Excellent and Good levels of ambient air quality reached 83.85% in four years, and Mild pollution was dominant (12.94%) when an over-standard phenomenon of pollutants occurred. Moreover, the main air pollutant in the study area increased from the single $PM_{10}$ before 2013 to the coexistence of $PM_{2.5}$, $O_3$, $PM_{10}$, and $NO_2$ after the implementation of new standards [44]. Among them, $PM_{2.5}$ accounted for the highest proportion, followed successively by $O_3$, $PM_{10}$, and $NO_2$ (Fig. 3(b)).
3.2. Monthly Variation Characteristics

Anthropogenic sources of PM in the atmospheric environment mainly include the combustion of fossil fuels, road and building dust, industrial production and emissions, and vehicle exhaust [9, 45–47, 49]. Owing to the different economic development modes and levels of cities, the contributions of various pollution sources to PM concentration in the ambient air of urban areas vary accordingly. In Nanchong City, agriculture is the major economic production, industry is not very developed, urban areas have big populations, and PM concentration is highly sensitive to biomass combustion and vehicle exhaust. The contributions of biomass combustion and vehicle exhaust to PM$_{2.5}$ accounted for 17.23% and 15.53%, respectively (data were collected from the analysis results of PM$_{2.5}$ source in Nanchong City in 2014–2016 [34]). The PM$_{2.5}$/PM$_{10}$ reached 66.83% in 2015–2018, which presented a small difference with PM$_{2.5}$/PM$_{10}$ in other cities like Jiaozuo City [50]. Additionally, the annual average concentration of NO$_2$ increased in the last four years, whereas the annual average concentration of SO$_2$ declined. The mean NO$_2$/SO$_2$ was as high as 2.80, which further proved the remarkable contributions of vehicle exhaust to PM$_{2.5}$.

When the pollution source is relatively stable, air pollution in cities is mainly determined by the diffusion, migration, and transformation of pollutants in air [47]. Low air pressure can lead to unstable meteorological conditions and easily cause blowing and raining while precipitation is an important mechanism in the process of wet removal [17, 51, 52]. Pollutants spread way much faster if the speed of wind goes up. Furthermore, higher temperature brings with them stronger atmospheric convective activity, which is beneficial for the migration and diffusion of pollutants [26, 51]. Fig. 4 shows that the monthly variations of PM$_{2.5}$, PM$_{10}$, CO, and
NO$_2$ from January to December all presented “U-shaped” distributions (Fig. 4(a), (b)). Given the close relationship between meteorological conditions and urban air pollution [53], in the current study, the correlations of major pollutants and various meteorological factors were discussed according to the Spearman correlation (Table S3). As shown in Table S3, temperature, precipitation, wind speed, and relative humidity all show significantly negative correlations with concentrations of PM$_{2.5}$, PM$_{10}$, CO, and NO$_2$, whereas air pressure shows positive correlations. These results in combination with Fig. 4 reveal that Nanchong City has high temperature, high wind speed, rich precipitations, low air pressure, and low relative humidity in summer (Fig. 4(d)–(f)), all of which are beneficial for the migration and diffusion of pollutants. The meteorological conditions in winter are the opposite and thus disadvantageous for the migration and diffusion of pollutants [35]. Owing to the significant seasonal variations in meteorological factors, monthly average concentrations of PM$_{2.5}$, PM$_{10}$, CO, and NO$_2$ presented “U-shaped” distributions. Table S3 also shows that there are highly positive correlations among PM$_{2.5}$, PM$_{10}$, CO, and NO$_2$. In particular, there is a strong correlation between PM$_{2.5}$ and PM$_{10}$ ($r = 0.969$, $p < 0.01$), and PM$_{2.5}$ is strongly correlated with CO and NO$_2$ ($r = 0.791$ and $r = 0.647$, respectively; $p < 0.01$). These results prove the close relations among PM$_{2.5}$, PM$_{10}$, CO, and NO$_2$ and show their strong homology and mutual transformation ability [5]. Monthly average concentrations of PM$_{2.5}$, PM$_{10}$, and CO during April–May and August–September increased to a small extent, which was mainly attributed to the combustion of straw. Nevertheless, the monthly concentration of NO$_2$ presented no fluctuations.

The monthly variation of O$_3$ concentration in Nanchong City presented an inverted “U-shaped” distribution in the last four years (Fig. 4(c)). Near-surface ozone (O$_3$) is the secondary
pollution from precursors like VOCs and NOx through photochemical reaction under solar radiation [15]. The high concentration of near-surface O₃ has strong oxidization and can greatly damage the physical health of humans, the ecosystem, and agricultural crops [54]. O₃ generally has weak negative correlations with other pollutants [13]. This is because substances like NOx and CO can promote the production of a secondary pollutant such as O₃ through photochemical reactions, and particles can generate an extinction effect, which is disadvantageous to the formation of O₃ [13, 55]. This outcome also corresponds with the significantly negative correlations of O₃ with PM₂.₅, PM₁₀, NO₂, and CO in Table S3. In addition, O₃ shows a significantly positive correlation with temperature (r = 0.541, p < 0.01) (Table S3). Under high temperature and strong solar radiation, NOx and VOCs easily develop photochemical reactions to produce O₃ [5, 56]. Wind also has a positive effect on O₃ [31, 57]; specifically, there is an obvious positive correlation between wind speed and O₃ (r = 0.44, p < 0.01) (Table S3). For this reason, O₃ concentration in spring and summer increases greatly, and the peak concentration occurs in July and August. This finding conforms to the research results of Zhang et al. [16]. Solar radiation in autumn and winter decreases [32]. Furthermore, horizontal visibility and the production rate of O₃ decline because of the increase in PM concentration, which significantly decreases O₃ concentration in autumn and winter [5, 58]. The “coal-to-gas” project was implemented in the main urban area of Nanchong City starting in 2000, and the total SO₂ concentration in air was relatively low [35]. SO₂ concentration in summer and autumn fluctuated slightly because of coal combustion in the urban areas, and the SO₂ that entered the air from the coal combustion in the suburbs easily diffused to the urban areas because of the higher wind speed in spring and summer.
The highest pollutant concentration in the main urban area of Nanchong City generally occurred in winter, followed by spring and autumn, and the lowest was in summer. This finding could be interpreted as follows: the main urban area of Nanchong City is at the bottom of a basin and has a low-lying terrain as well as uneven distributions of meteorological factors among four seasons. According to Fig. 4f, there are few precipitations and low wind speed in winter but high quiet wind frequency. There are also weak illuminations, short illumination hours, and a strong and thick thermal inversion layer in winter [51], making pollutants in air difficult to diffuse [58]. Along with the effect of other factors (e.g., burning of coal and wood during the heating period), PM$_{2.5}$, PM$_{10}$, SO$_2$, CO, and NO$_2$ in the study area were generally high in winter. On the contrary, summer is conducive to the diffusion and settlement of pollutants [51] due to the high temperature, high wind speed, strong atmospheric convective activity, shortening duration of thermal inversion layer, strengthened atmospheric turbulent mixing and vertical convection [52], low air pressure, and abundant precipitations. Table S3 shows that AQI has significantly negative correlations with temperature, precipitation, wind speed, relative humidity, and horizontal visibility ($r = -0.429$, $-0.414$, $-0.352$, $-0.132$, and $-0.0549$, respectively; $p < 0.01$) and a positive correlation with air pressure ($r = 0.417$, $p < 0.01$). To sum up, high temperature, low air pressure, high wind speed, and high relative humidity are beneficial to the dilution and diffusion of pollutants, and air quality is the collaborative consequence of various meteorological factors and pollution emissions by human activities. In the study area, temperature, air pressure, precipitation, and wind speed greatly influence air quality; in comparison, the effect of humidity on air quality is relatively small.
3.3. Diurnal Variation Characteristics

In view of the shapes of profiles, diurnal variations of PM$_{2.5}$, PM$_{10}$, NO$_2$, and CO show evident bimodal distribution (Fig. 5(a)–(c), (e)). The two peaks occur after rush hours in the morning and evening. The first peak occurs after the rush hour in the morning when the mixing layer has not been developed completely. This period experiences poor turbulent diffusion in daytime [59] and large traffic flows, which increase PM, NO$_2$, and CO significantly. As time goes on, solar radiation and atmospheric turbulence activity are strengthened in the afternoon, when the diffusion capacity of pollutants reaches the maximum level [24, 53]. As a result, the concentrations of PM$_{2.5}$, PM$_{10}$, NO$_2$, and CO decrease. Subsequently, the height of the boundary layer decreases and a stable boundary layer is formed gradually at nightfall, weakening the atmospheric diffusion conditions [60]. Moreover, influenced by rush hours in the evening, the concentrations of PM$_{2.5}$, PM$_{10}$, NO$_2$, and CO have their second peaks before 24:00. The second peak concentrations are significantly higher than the first peak concentrations. Meanwhile, SO$_2$ concentration climbs up substantially. Different from PM$_{2.5}$, PM$_{10}$, NO$_2$, and CO, the diurnal variation of SO$_2$ concentration presents a single-peak distribution (Fig. 5(d)). However, the diurnal variation distribution of SO$_2$ is different from the bimodal distribution in some studies [25, 57], due to the fact that Nanchong City is a large agricultural city with underdeveloped industries, and the phenomenon of morning and evening peak caused by human activities is not obvious. SO$_2$ concentration in the evening is substantially higher than that in the daytime because of the existence of SO$_2$ in the evening and the better conditions for pollutant diffusion in the daytime than in the evening [60]. As a result, the lowest SO$_2$ concentration is observed at 16:00. Diurnal variation characteristics of NO$_2$/SO$_2$ were analyzed (Fig. 5(g)). NO$_2$/SO$_2$ presents...
an evident peak during the morning peak of NO₂. This further proves that the environmental
effect of mobile source emissions is stronger than that of fixed source emissions during rush
hours in the morning. Concentrations of PM₂.₅, PM₁₀, NO₂, and CO are mainly influenced by
vehicle exhausts. Therefore, these concentrations rise in the period with great vehicle activities
and then decrease in rest periods. SO₂ concentration is mainly influenced by atmospheric
diffusion conditions. Generally, these conditions are relatively poor from evening to the next
morning but good from late afternoon to early evening, resulting in a single-peak distribution in
the diurnal variation curve of SO₂.

Diurnal variation of O₃ presents a single-peak distribution, which is opposite the diurnal
variation of SO₂ (Fig. 5(f)). Precursors produced by human activities in daytime, including
VOCs and NOₓ, generate O₃ through photochemical reactions. Solar radiation is the strongest in
the afternoon [16], and O₃ concentration reaches its peak at about 16:00. However, O₃
concentration in the evening declines significantly because of the absence of solar radiation and
the titration effect of NO to O₃ [61, 62]. NO₂ can not only further promote the formation of
particulates by producing nitrates [5] but also produce O₃ through photochemical reactions [15].
Hence, the variations of PM₂.₅ and PM₁₀ lag behind the variation of NO₂ by about 1 hour, and the
variation of O₃ lags behind by about 2 hours. Abdul-Wahab et al. [63] found that solar levels
contribute considerably to elevated daytime O₃ concentrations with NO, whereas NO₂ is the
major stimulus at night. In terms of diurnal variation of PM, NO₂, SO₂, CO, and O₃, there is a
clear variation in the level of pollutant concentration, which obviously follows the diurnal
variation of atmospheric temperature and main anthropogenic and traffic activities.
According to seasonal differences in diurnal distributions of the six elements, concentrations of PM$_{2.5}$, PM$_{10}$, NO$_2$, and CO in summer are significantly lower than those in winter. This outcome is consistent with existing research results [29] and is mainly determined by seasonal differences of atmospheric diffusion conditions [64]. (Fig. 4(d)–(f)) showed that the meteorological factors varied with the seasonal changes in Nanchong City. The synoptic model of pollution is generally related with relatively high surface pressure, low temperature, high relative humidity, and low wind speed [51]. Meteorological conditions in Sichuan Basin in winter are conducive for the formation of disadvantageous atmospheric diffusion conditions [65]. The high temperature in summer can facilitate atmospheric turbulence, thus increasing the diffusion of pollutants. Moreover, wet removal of pollutants increases with the increase in precipitation, which can lower pollutant concentrations [8, 32]. The variation of O$_3$ is the opposite. The production rate of O$_3$ is mainly determined by solar radiation intensity [5]. O$_3$ concentration increases in spring and summer due to the strengthened solar radiation but decreases in winter because of the weakening solar radiation [51]. Since human activity is affected by daytime and nighttime, variations of the six elements during the first peak in winter lag behind those in spring and summer, but the variations during the second peak are earlier (for 1–2 h).

A day and night comparison was conducted between the concentration of six elements in spring and summer and in autumn and winter. During the day, especially in the afternoon, the difference between spring and summer concentration and autumn and winter concentration increases, whereas the difference in nighttime concentration value decreases. This outcome is attributed to the great seasonal differences in terms of atmospheric diffusion conditions during
daytime (08:00–20:00). Pollutant concentrations in spring and summer when there are good atmospheric diffusion conditions decrease greatly, thus increasing the differences compared to those in autumn and winter. Owing to the sharp reduction of emission sources, the concentrations of various pollutants at night are closer to the environmental background values, and the nocturnal diffusivity of different seasons is smaller than that of the daytime; hence, the nocturnal difference decreases. However, the concentration of O$_3$ is mainly determined by the intensity of solar radiation [32], which is high during the day and low at night. In addition, there is high relative humidity in Sichuan Province in autumn and winter [60] (Fig. 4(e)), causing SO$_2$ and NO$_2$ to generate heterogeneous reactions easily and thus be consumed. Hence, the seasonal difference of NO$_2$ decreases significantly at night compared to that during daytime, and SO$_2$ concentration in autumn and winter is even lower than that in spring and summer.

3.4. Interaction between O$_3$ and PM$_{2.5}$

Currently, the composite air pollution is becoming more prominent in China [66, 67]. PM$_{2.5}$ and O$_3$ have become two major pollutants in composite air pollution [68]. Some studies have pointed out that concentrations of PM$_{2.5}$ and O$_3$ are related to the death rate and many health issues [69, 70]. Hence, the relations and interaction between PM$_{2.5}$ and O$_3$ have attracted the attention of scholars [71–73]. The monthly distribution patterns of daily variations of PM$_{2.5}$ and O$_3$ in Nanchong City are shown in Fig. 6. From April to August, the maxima of O$_3$ concentration are achieved from late afternoon to early evening while the corresponding PM$_{2.5}$ is the minimum. PM$_{2.5}$ has an obviously negative correlation with O$_3$ ($r = -0.381, p < 0.01$) (Table S3). In other
periods, the correlation is not obvious. Hence, the relationship between PM$_{2.5}$ and O$_3$ is further studied according to their interaction.

3.4.1. Effects of PM$_{2.5}$ on O$_3$

The effects of PM$_{2.5}$ on O$_3$ are mainly determined by the production rate of O$_3$ under three PM$_{2.5}$ concentrations. As shown in Fig. 7(a) and 7(b), O$_3$ concentration decreases significantly with the increase in PM$_{2.5}$ concentration. Furthermore, O$_3$ concentration presents consistent variation trends under three PM$_{2.5}$ concentrations. Specifically, the absolute variation rate of O$_3$ is low during 24:00–08:00, which centers on consumption. However, O$_3$ concentration subsequently increases greatly. The variation rate of O$_3$ reaches the maxima at 12:00 (Fig. 7(a)). The growth rate of O$_3$ concentration when the PM$_{2.5}$ concentration meets the standard (PM$_{2.5}$ $<$ 75 μg/m$^3$) is the highest. Before 08:00, the temperature is low, the solar radiation is weak, the O$_3$ generation rate is low and the formation process is not significant. Over time, the temperature rises after sunrise and solar radiation increases, leading to a significant increase in ozone formation and its concentration reaches the peak at 16:00 (Fig. 7(b)). Subsequently, O$_3$ concentration begins to decrease continuously and reaches the minimum at nightfall. When there is PM$_{2.5}$ pollution (PM$_{2.5}$ $>$ 75 μg/m$^3$), the production rate of O$_3$ is clearly relatively low. These results demonstrate that PM$_{2.5}$ can inhibit the generation of O$_3$ in Nanchong City, and such inhibition effect is strengthened greatly when there is PM$_{2.5}$ pollution (PM$_{2.5}$ $>$ 75 μg/m$^3$) during daytime.

The main effects of PM$_{2.5}$ on O$_3$ are the direct radiation effects and the heterogeneous effects [74]. The increase of aerosol concentration will increase the consumption of O$_3$ precursors (NOx) by heterogeneous reactions, which will lead to the decrease of O$_3$
concentration [75]. Furthermore, the increase of aerosol concentration can cause significant loss of O$_3$ concentration, which may be due to the direct radiative forcing effect of aerosol [76]. On the one hand, PM is rich in BC, sulfate, nitrate, and other extinction components, all of which can greatly weaken horizontal visibility [13]. On the other hand, PM can change the optical thickness of clouds by influencing the microphysical process, thus further affecting solar shortwave radiation on the surface [77]. Accordingly, high-concentration PM can inhibit the production of O$_3$ by weakening the near-surface photochemical activity.

3.4.2. Effects of O$_3$ on PM$_{2.5}$

As shown in Table S3, there has evident correlation between PM$_{2.5}$ and CO ($r = 0.791, p < 0.01$). Furthermore, CO is a primary pollutant with stable chemical properties, the atmospheric oxidation is relatively low when the O$_3$ concentration is low (O$_3 < 100$ μg/m$^3$ in this study) and most PM$_{2.5}$ are primary pollutants. According to the Formula (2) mentioned above, the primary PM$_{2.5}$ concentration under different O$_3$ concentrations can generally be estimated according to $(CO)_T \times (PM_{2.5}/CO)_L$, thus enabling the estimation of the secondary PM$_{2.5}$ concentration. The effects of O$_3$ on PM$_{2.5}$ was studied by assessing the proportion of secondary particulate matter at different levels of O$_3$ concentration. The calculated results are shown in Fig. 7(c). The primary PM$_{2.5}$ concentrations are 34.52, 33.87 μg/m$^3$, and 36.48 μg/m$^3$ when the O$_3$ concentration is 100–160, 160–200, and > 200 μg/m$^3$, respectively. Such small differences in primary PM$_{2.5}$ concentrations indicate that local emission sources are relatively stable. Under this circumstance, the secondary PM$_{2.5}$ concentrations are 0.98, 5.96, and 11.90 μg/m$^3$, which account for 2.75%, 14.96%, and 24.60%, respectively. The concentration of secondary PM$_{2.5}$ increases significantly
with the increase in \( O_3 \) concentration. In China, secondary particulates are typically generated by oxidative reaction [78]. With its strong oxidation property, \( O_3 \) is the major oxidizing agent in the atmosphere, and it can cause indirect effects on the formation of secondary particulates [57]. The concentration change of secondary PM\(_{2.5}\) is obvious, indicating that atmospheric oxidation is strengthened with the increase in \( O_3 \) concentration, which in turn increases the generation of secondary PM\(_{2.5}\). To sum up, \( O_3 \) can promote the formation of PM\(_{2.5}\).

Generally speaking, the study concerns the interaction between PM\(_{2.5}\) and \( O_3 \) plays an important role in air pollution control [74, 75, 79, 80]. Specifically, particulate matter has a significant attenuation effect on downward shortwave radiation (DSR), and the relative humidity could enhance the attenuation effect, resulting in a decrease in \( O_3 \) concentration [75]. Diffusion conditions are unfavorable in winter, the concentrations of gaseous pollutants and aerosols increased obviously [75], leading to the significant attenuation effect on DSR. In winter, the inhibition effect of PM\(_{2.5}\) on \( O_3 \) dominates the change of urban air composite pollution in Nanchong. However, during summer, precipitation is abundant, the wet precipitation of particulate matter is remarkable, and the strong radiation and high temperature in summer will enhance the photochemical reaction, which is beneficial to the formation of \( O_3 \). As a result, the formation of secondary particles is easy to be promoted. Therefore, different measures should be taken in the treatment of atmospheric pollution according to seasonal variations in these two main pollutants. And PM\(_{2.5}\) emission should be controlled strictly in winter, while in summer, the sources of \( O_3 \) should be controlled vigorously [79].

4. Conclusions
Overall, the air quality of the main urban area of Nanchong City reached the standard during 2015–2018 and improved continuously. Nowadays, the continuous over-standard of annual average PM$_{2.5}$ and increasing O$_3$ concentration are the two major challenges to air quality.

The monthly average mass concentrations of PM$_{2.5}$, PM$_{10}$, NO$_2$, and CO are high in winter but low in summer, showing a “U-shaped” distribution pattern. Moreover, the correlations among these pollutants are significant and positive, whereas the distribution of O$_3$ is the opposite and is negatively correlated with other pollutants. Temperature, wind speed, air pressure, and precipitation influence air quality greatly.

Diurnal variations of SO$_2$ and O$_3$ present opposite single-peak distribution patterns. They are mainly influenced by atmospheric diffusion conditions and solar radiation, respectively. Diurnal variations of PM, NO$_2$, and CO present bimodal distribution due to the morning and evening rush hours. According to our analysis, mobile sources make greater contributions to air pollution compared to fixed sources.

There is an obvious interaction between PM$_{2.5}$ and O$_3$. The increase in PM$_{2.5}$ concentration, especially when it exceeds the standard (> 75 μg/m$^3$), will decrease the photochemical activity in the atmosphere and the rate of O$_3$ production. However, O$_3$ can promote the formation of secondary PM$_{2.5}$ by increasing atmospheric oxidation. Overall, PM$_{2.5}$ emission should be controlled strictly in winter, while in summer, the sources of O$_3$ should be controlled vigorously. In addition, the study area should increase administration efforts to control anthropogenic source emissions like mobile sources.

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Author Contributions
X.L. (M.D) wrote and revised the manuscript. Q.Z. (Postgraduate Student) wrote and revised the manuscript. Y.F.Q. (M.D) and J.H. (M.D) made significant contributions to data acquisition, analysis, and interpretation. D.Y.L. (M.D), P.Z. (Postgraduate Student), and X.Y. (Postgraduate Student) helped organize the manuscript data. Q.M.Q. (Professor) and Y.X.L. (Professor) made key changes to important academic content and were responsible for the final revision.

References


Fig. 1. Map of main urban area of Nanchong City.

Fig. 2. Distribution of daily mean AQI in the study area during 2015–2018. (Notes: These four levels (I, II, III, IV) are corresponding to Excellent, Good, Mild pollution, Moderate pollution, respectively.)
Fig. 3. (a) Number of days of air pollution at different levels in the study area during 2015–2018, (b) Percentage of main pollutants in different stages. (Notes: main pollutant is the air pollutant with the maximum IAQI when the AQI is higher than 100 at the day)

Fig. 4. Monthly variations of pollutants (a–c) and meteorological factors (e–f).

T, temperature; HV, horizontal visibility; AP, air pressure; RH, relative humidity; P, precipitation; WS, wind speed.
Fig. 5. Diurnal distribution characteristics of six elements of ambient air quality and NO$_2$/SO$_2$ in spring and summer as well as autumn and winter in the study area.

Fig. 6. Monthly distribution of daily variations of O$_3$ and PM$_{2.5}$. 
Fig. 7. (a) Hourly variation rate of $O_3$ under different PM$_{2.5}$ concentrations, (b) Diurnal variation of $O_3$ under different PM$_{2.5}$ concentrations, (c) Percentages of primary and secondary PM$_{2.5}$ under different $O_3$ concentrations in Nanchong City.