

CHARACTERISTICS AND INFLUENCING FACTORS OF THE NEAR-GROUND OZONE CONCENTRATIONS IN CHANGSHA, A TYPICAL CITY IN CENTRAL AND SOUTHERN CHINA

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Abstract. This study aimed to preliminarily explore the distribution characteristics of the ozone (O₃) pollution period in 2021 in Changsha, which is a typical city in central and southern China, and the differences in reasons for ozone and other pollutions were also investigated. The study was based on the hourly environmental monitoring and meteorological data in 2021 provided by the Ecological Environment Monitoring Center and Meteorological Observatory of Hunan Province. The effects of topography, precursors, meteorological conditions, and other factors on the O₃ concentration were analyzed. The results showed that the overall air quality of 14 environmental monitoring stations in Changsha in 2021 was less affected by sulfur dioxide, nitrogen dioxide (NO₂), and carbon monoxide, and principally affected by particulate matter and O₃. Among the 14 environmental monitoring stations, the duration of pollution due to O₃ was in the range of 0–29 days, with a maximum concentration of 252 µg/m³; the daily O₃ concentrations were in the range of 29–94 µg/m³, showing “unimodal” trends in general; and the monthly average O₃–8 h (the daily maximum 8-h O₃ concentrations) concentrations were in the range of 44–149 µg/m³, showing “bimodal” trends in general. Generally speaking, compared with the provincial control sites, the ozone concentration of the national control sites was higher, and the urban areas were higher than the suburbs. The O₃ concentrations were ranked in the following order: summer > autumn > spring > winter, and the urban area was affected to a larger extent by the emission. The concentrations of O₃ and NO₂ varied in opposite trends. The O₃ concentration exhibited a typical “inverted U-shaped” profile, while that of NO₂ substantially exhibited a “U-shaped” profile. The O₃ concentration was significantly positively correlated with the daily average wind speed and ambient temperature but negatively correlated with the wind direction, wind pressure, and humidity. The following conditions promoted the generation of O₃ in Changsha: ambient temperature of around 30°C, relative humidity of around 50%, and wind speed of 0.5–2.0 m/s. These findings are beneficial for the scientific prediction, warning, and control of O₃ pollution in the central and southern regions of China.

Keywords: *Changsha, distribution characteristic, causative factors, meteorological factor, ozone pollution*

Introduction

In the last decades, the rapid development of the economy has significantly deteriorated energy consumption, air pollutant emission, and air pollution worldwide (Li et al., 2013; Wang et al., 2022; Zhao et al., 2013). The troposphere ozone (O₃) has been well recognized to have natural and secondary atmospheric sources. The former is due to the transfer of O₃ from the stratosphere to the troposphere. The latter is attributed

to the emissions of nitrogen oxides (NO_x) and volatile organic compounds (VOCs) from natural and artificial sources such as coal combustion, automobile exhaust, chemical industry, and petroleum industry. Photochemical reactions occur between NO_x and VOCs to produce O₃ under solar conditions (Feng et al., 2018). O₃ has been the primary atmospheric pollutant in summers, and the sources and precursors have a significantly nonlinear relationship (Dentener et al., 2006; Sillman, 1999). Besides the aforementioned factors, the change in O₃ concentration has also been affected by natural meteorological conditions (Fujita et al., 2016; Li et al., 2021). Concentrated O₃ pollution events are usually related to meteorological factors, such as high temperature, low wind speed, and low relative humidity (RH), and typical atmospheric circulation modes, such as anticyclone and high-pressure systems because these factors enhance the chemical production and accumulation of O₃ in the boundary layer (Shen et al., 2015; Xu et al., 2011; Zhao et al., 2016; Yu et al., 2020). Moreover, the meteorological conditions also alter the O₃ exchange between the stratosphere and the troposphere, thereby affecting the O₃ concentration in the lower troposphere (Li et al., 2013; Lin et al., 2015). O₃ is principally removed from the troposphere through chemical reactions, and the VOCs produced by plants also significantly contribute to near-ground O₃ (Yao et al., 2021). In the last decades, extremely high concentrations of aerosols (particulate matter PM₁₀ and PM_{2.5}) have been observed in industrialized areas around the world, which had a significant impact on the O₃ concentration through heterogeneous reactions and influencing photolysis rates (Fu et al., 2019). Therefore, the O₃ present in the troposphere is a secondary pollutant and an important greenhouse gas with ultra-strong oxidative toxicity (Wang et al., 2016).

Currently, many studies have reported on the spatiotemporal characteristics, chemical precursor sources, meteorological factors, influence of terrain characteristics, and other influencing factors of O₃ in the ambient pollution of different cities, but have rarely analyzed the changes and differences among multiple stations (Yang et al., 2021; Kong et al., 2022; Quan et al., 2022; Liu et al., 2020; Sun et al., 2016). The central southern region is one of the developed agricultural regions in China, and Changsha is an important new first-tier city. In the last decades, rapid urbanization, industrialization, and agricultural modernization have led to a continuous increase in the number of motor vehicles and the quantity of coal combustion products with high energy consumption in the industry. The pollution problems due to PM_{2.5} and O₃ are prevalent in the entire Hunan Province (Liu et al., 2022). However, the deteriorating trend of O₃ pollution has not been effectively alleviated. Therefore, O₃ pollution in the major cities in the central and southern regions has become a serious concern. In the past, O₃ pollution was mainly distributed in Beijing, Tianjin, Hebei, the Yangtze Delta, and the Pearl River Delta urban regions, and the research on major cities or regions, particularly in Changsha, with their unique geographical and climatic characteristics, was not enough. Therefore, this study aimed to analyze and preliminarily investigate the characteristics of O₃ concentration and the causes of pollution in each pollution period in 2021 in Changsha. The similarities and differences in the characteristics of O₃ pollution in Changsha and other regions as well as the changes in O₃ concentration between stations were analyzed, and the impact of terrain, precursors, and meteorological conditions on O₃ concentration was clarified, to establish scientific scaffolds for the prediction, warning, and control of ozone pollution in this city. The purposes of this study were as follows: (a) Analyze the current situation and problems of O₃ pollution in Changsha and clarify the pollution degrees of the six standard pollutants; (b) investigate the spatiotemporal variation

characteristics of O₃ concentrations in 14 environmental monitoring stations in Changsha; (c) analyze the relationships between the primary precursors and O₃; and (d) clarify the correlation between changes in O₃ concentration and meteorological factors.

Materials and methods

Overview of the research area

Changsha is located in central China, north of eastern Hunan Province (27°51'—28°41'N, 111°53'—114°15'E), along the lower reaches of the Xiangjiang River, and on the western edge of the Changsha Basin. It spans 230 km from east to west, 88 km from north to south, covering an area of 11,819 km². Its population density is high, with a total population of more than 7.9 million. It has a mild subtropical monsoon climate with abundant precipitation. Its rainy season is hot, and all four seasons are well-defined. The annual average temperature is 17.2°C, and the average yearly precipitation amounts to 1361.6 mm (Jia et al., 2017).

The study sourced online atmospheric observation data from 10 national and 4 provincial control air automatic monitoring stations in Changsha. The national control stations (Environmental Protection Bureau in the Gaokai District, Hunan Normal University, Hunan University of Chinese Medicine, Environmental Protection Bureau in the Tianxin District, New Railway Station, Mapoling, Wujialing, Shaping, Environmental Protection Bureau in the Yuhua District, and Environmental Protection Bureau in the Economic Development Zone) were concentrated in the main urban area of the city. In contrast, the provincial control stations (Environmental Protection Bureau in the Ningxiang City, Management Committee in the Economic Development Zone of Wangcheng District, Changsha County Government, and Environmental Protection Bureau in the Liuyang City) were distributed in the suburb. The study period was from January 1, 2021, to December 31, 2021 (*Fig. 1; Table 1*). In this study, the seasons were divided based on the regulations of the China Meteorological Administration (QX/T152-2012): spring (March and May), summer (June and August), autumn (September and November), and winter (December and February). Each administrative region in Changsha had a monitoring station. These locations were selected to reflect the diversity of potential sources of variability of air pollution in Changsha, such as population density (882 people/km²), transportation environment, industry, and geographical and climatic conditions. Therefore, the data thoroughly reflected the overall O₃ pollution situation in Changsha.

Data source and preliminary processing

The hourly monitoring data of O₃, PM_{2.5}, PM₁₀, nitrogen dioxide (NO₂), sulfur dioxide (SO₂), and carbon monoxide (CO) in the 10 national and 4 provincial control stations of Hunan Provincial Ecological Environment Monitoring Center in 2021, as well as the meteorological data and observation data (temperature, pressure, RH, wind speed, and wind direction) of Hunan Provincial Meteorological Station in 2021, were taken as the data source. The missing or abnormal data were fixed by linear interpolation. According to the standards “Environmental Air Quality Standard” (GB 3095-2012) and “Technical Specification for Environmental Air Quality Assessment (Trial)” (HJ 663-2013), the daily maximum 8-h dynamic average concentration value of O₃ (O₃-8 h) and the hourly average concentration value of O₃ (O₃-h) are the common

O₃ evaluation indicators. The O₃-8 h index was used to assess the O₃ concentration and excessive emissions in this study. Excel and Origin 2021 were used to analyze, process, evaluate, and plot the relevant data.

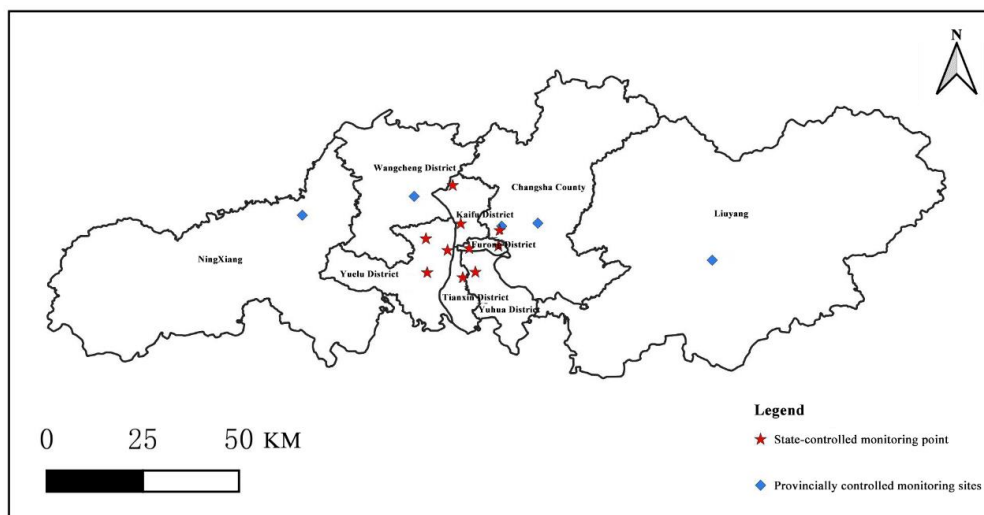


Figure 1. Spatial distribution of O₃ monitoring stations in Changsha

Table 1. Names and abbreviations of 14 monitoring stations in Changsha

No	Point name	Abbreviation
1	New Railway Station	HCXZ
2	Hunan Normal University	HNSF
3	Shaping	SP
4	Hunan University of Chinese Medicine	HNZYY
5	Environmental Protection Bureau of Economic and Technological Development Zone	JKHB
6	Mapoling	MPL
7	Environmental Protection Bureau of Tianxin District	TXHB
8	Wujialing	WJL
9	Environmental Protection Bureau of Yuhua District	YHHB
10	Environmental Protection Bureau of Gaokai District	GKHB
11	Ningxiang Environmental Protection Bureau	NXHB
12	Management Committee of Wangcheng District Economic Development Zone	WCJK
13	Changsha County Government	CCX
14	Liuyang Environmental Protection Bureau	LYHB

Results and discussion

Current situation of atmospheric environment pollution in Changsha in 2021

According to the quality required by the environmental functional zone defined in Section 4 of the “Environmental Air Quality Standard” (GB 3095-2012) (Table 2), the threshold values of level-2 standards for the annual average concentrations of SO₂, NO₂, PM₁₀, and PM_{2.5} in region II were 60, 40, 70, and 35 µg/m³, respectively. The threshold value of 24-h average CO concentration was 4 mg/m³. In 2021, the annual average concentrations of SO₂, NO₂, and PM₁₀ pollutants at the 14 environmental monitoring

stations in Changsha did not exceed the threshold values of level-2 standards (*Fig. 2*), but the PM_{2.5} concentrations in most of the stations exceeded the threshold value and were significantly higher than those of the other pollutants. Only the values in Environmental Protection Bureaus in the Ningxiang and Liuyang cities did not exceed the threshold value. The average annual PM_{2.5} concentrations in other monitoring stations were in the range of 37–46 µg/m³, and the average annual PM₁₀ concentration in each station was in the range of 44–59 µg/m³, which were significantly higher than those of other pollutants. The average annual concentrations of SO₂, NO₂, and CO were relatively low, without exceeding the threshold values of level-2 standards. This indicated that SO₂, NO₂, and CO were not the dominant influencing factors of air quality in Changsha in 2021.

Table 2. Concentration limits of basic items of ambient air pollutants

No	Pollutant item	Meantime	The limit of concentration		Unit
			First-order	Second-order	
1	SO ₂	Annual mean	20	60	µg/m ³
		24-h average	50	15	
		1-h average	150	500	
2	NO ₂	Annual mean	40	40	
		24-h average	80	80	
		1-h average	200	200	
3	CO	Annual mean	4	4	mg/m ³
		24-h average	10	10	
4	O ₃	The daily maximum 8-h average	160	200	µg/m ³
		1-h average	160	200	
5	PM ₁₀	Annual mean	40	70	
		24-h average	50	150	
6	PM _{2.5}	Annual mean	15	35	
		24-h average	35	75	

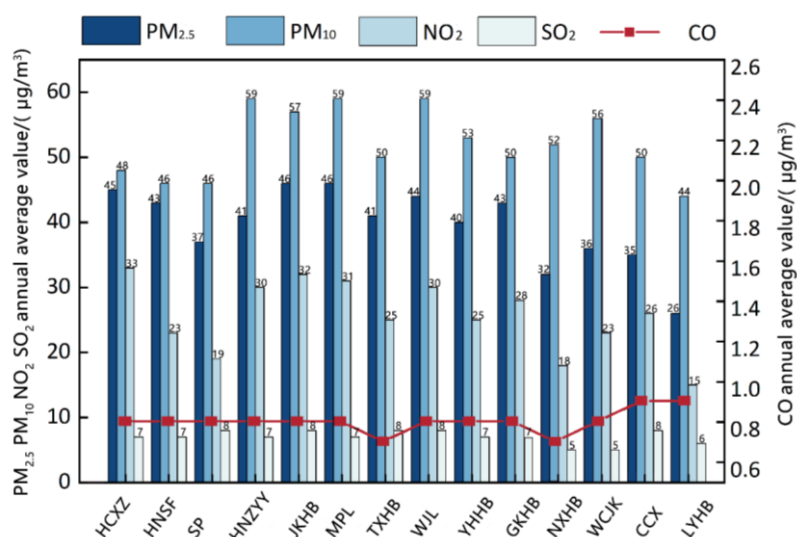


Figure 2. Annual mean values of pollutant concentrations in the monitoring stations in Changsha in 2021

Additionally, the number of O₃ pollution days in the 14 environmental monitoring stations in Changsha in 2021 was in the range of 0–29 days (Fig. 3). The difference among these stations was obvious. Hunan Normal University, Shaping; Environmental Protection Bureau of Economic Development Zone, Mapoling; Environmental Protection Bureau of Tianxin District, Wujialing; and Environmental Protection Bureau of Gaokai District all reported more than 20 pollution days. In contrast, the Environmental Protection Bureaus of Ningxiang and Liuyang reported zero pollution days. The ratios of pollution days in these 14 environmental monitoring stations with PM_{2.5} as the dominant pollutant accounted for 1.9%–13.1%. Notably, urban areas experienced significantly more pollution days than the suburbs. Among these stations, the dominant pollutant in the New Railway Station, Environmental Protection Bureau of Economic and Technological Development Zone, Mapoling, Wujialing, and Environmental Protection Bureau of Gaokai District all recorded over 40 pollution days with PM_{2.5} as the primary pollutant. However, for all these stations, the dominant pollutant did not exceed 10 days. According to the previous analysis results, the seriously polluted stations among the 14 monitoring stations in Changsha were located in the urban area, which might be ascribed to their terrains. The northeast and northwest regions of Changsha are surrounded by mountains, the central terrain is relatively flat, and hillocks are distributed in most of the urban region. These special terrains led to the concentration of particulate matter in the urban area with poor diffusion performance. The volatile organic compounds in each monitoring site were mainly alkanes, followed by aromatic hydrocarbons and olefins. The main sources of hydrocarbon compounds in Changsha urban site were liquefied petroleum gas, motor vehicle exhaust emissions, and organic solvents. VOCs, as the precursors of O₃ and secondary organic aerosol (SOA), are important in the formation of air pollution (Fu et al., 2021; Hui et al., 2019). Therefore, particulate pollution was more serious in the urban region than in the suburbs. Additionally, the rising trend of O₃ pollution was not effectively alleviated, indicating that Changsha was affected by both ozone and particulate matter in 2021. In contrast, only 8 days of particulate matter pollution took place in the provincial control station of Liuyang Environmental Protection Bureau, and the excess of O₃ concentration was not observed.

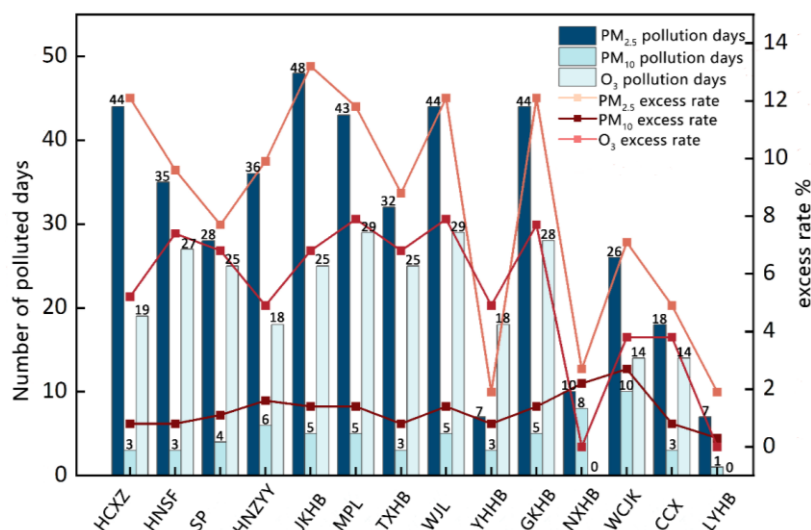


Figure 3. Days of pollution and ratios of pollution days in the monitoring stations in Changsha in 2021

Temporal variation characteristics of O₃ in the monitoring stations in Changsha in 2021

Daily variation characteristics

The daily variation characteristics of hourly O₃ concentrations in these 14 environmental monitoring stations in Changsha in 2021 are depicted in *Figure 4*. The hourly O₃ concentrations represent the arithmetic mean values of O₃ concentrations within 1 h in each monitoring station. Generally speaking, the data showed an obvious “unimodal” trend, with daytime concentrations much higher than nighttime concentrations. The daily concentrations were in the range of 29–94 µg/m³, and the daily O₃ concentrations varied by following these three stages. In the first stage, O₃ accumulated, when the tropospheric temperature was low without the solar radiation. The titration effect of NO was weak due to the low lighting intensity. From 8:00 to 10:00, the concentration of O₃ commenced to dramatically increase, and this was the O₃ generation stage. Subsequently, as the lighting further intensified, the photochemical reaction rate to give O₃ improved and the rate reached a maximum between 14:00 and 17:00. The changes in the O₃ concentrations of these stations were different. The O₃ concentration changes in the provincial control monitoring stations were much more obvious than those in the national control monitoring stations. The daily variation characteristics of O₃ concentrations were obvious in the national control stations, including Hunan Normal University, Shaping; Environmental Protection Bureau of the Economic Development Zone, Mapoling; and Wujialing. The O₃ concentrations in the provincial control stations were ranked in the following order: Ningxiang Environmental Protection Bureau > Wangcheng District Economic Development Zone Management Committee > Changsha County Government > Liuyang Environmental Protection Bureau. The lowest O₃ concentration in Liuyang Environmental Protection Bureau was possibly because of its special geographical location, mountainous and superior natural environment, and relatively weak pollution from traffic and other emission sources. This result was substantially consistent with the analysis results of daily O₃ concentration variation trends in Zhaoqing and Guangzhou Cities observed by Weng et al. (2021) and Huang et al. (2018).

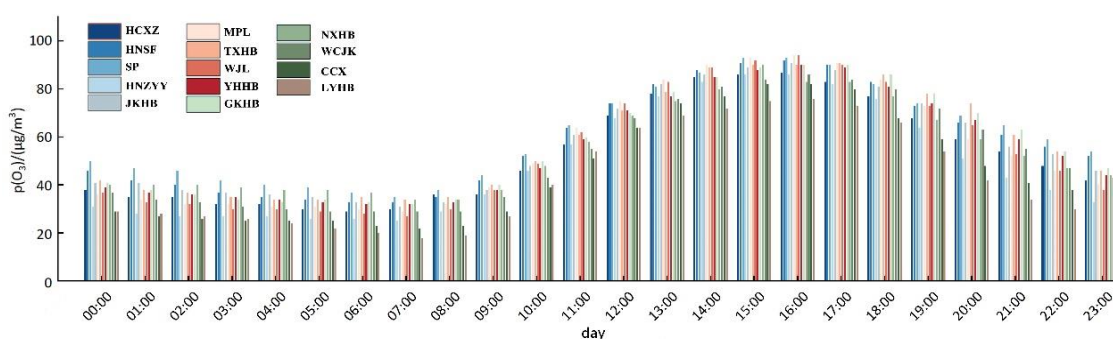


Figure 4. Variations in hourly O₃ concentrations in the monitoring stations in Changsha in 2021

Monthly and seasonal variation characteristics of O₃–8 h values

The monthly variation characteristics of O₃–8 h values in the 14 environmental monitoring stations in Changsha in 2021 are illustrated in *Figure 5*, where the O₃–8 h

values represent the arithmetic mean values of the daily maximum 8-h O₃ concentrations. The monthly average O₃-8 h concentrations in Changsha in 2021 were in the range of 44–149 µg/m³, and the O₃-8 h data showed a “bimodal” pattern over time. The first peak occurred in March to June, with a maximum of 127 µg/m³. Although the O₃-8 h values slightly decreased from June to August, the profiles generally showed an upward trend. The second peak occurred from August to September, with a maximum of 149 µg/m³. The possible reason for the two peaks was that the higher temperature during the day was conducive to the formation of ozone. From October, the solar ultraviolet radiation gradually weakened, the temperature gradually declined, and the cold-air outbreaks commenced. In this stage, the PM_{2.5} emissions reached their maximum, and the concentrated PM_{2.5} weakened the near-ground photochemical reaction rate to generate O₃, resulting in the low O₃-8 h values, which occurred in January, February, March, and December. In detail, the O₃-8 h values in all the stations in different months exhibited certain spatiotemporal characteristics. The O₃ concentrations were higher in the national control monitoring stations than in the provincial control monitoring stations. The O₃ concentration reached a maximum of 149 µg/m³ in the Mapoling station in September, whereas it reached a maximum of 101 µg/m³ in the Ningxiang Environmental Protection Bureau station. The difference was 48 µg/m³. Based on the data of *Table 3* and *Figure 5*, the number of days with O₃ as the dominant pollutant in each station in the months with high O₃ concentrations was relatively large, and the ratios of days with O₃ as the dominant pollutant were the highest in September. Except for the Ningxiang and Liuyang Environmental Protection Bureaus, the other monitoring stations had 14–29 days with O₃ as the dominant pollutant. From November to March of the next year, the number of days with O₃ as the dominant pollutant was small, even zero, indicating that the high concentration of O₃ at a specific site was controlled by various factors such as terrain, primary emissions, photochemical reactions, and so forth. The formation mechanism of O₃ was more complex than that of other pollutants (Fu et al., 2021; Li et al., 2017).

Table 3. The number of ozone pollutant days in each month of Changsha monitoring site in 2021

Station name	January	February	March	April	May	June	July	August	September	October	November	December
HCXZ	–	–	–	1	1	5	2	3	7	–	–	–
HNSF	–	–	–	–	2	6	2	3	14	–	–	–
SP	–	–	–	1	2	6	2	3	11	–	–	–
HNZYY	–	–	–	–	2	6	1	2	7	–	–	–
JKHB	–	–	–	1	1	6	3	3	11	–	–	–
MPL	–	–	–	–	3	6	4	4	12	–	–	–
TXHB	–	–	1	–	1	5	1	3	12	–	1	1
WJL	–	–	–	1	2	8	3	3	11	–	–	1
YHNB	1	–	–	–	–	4	1	3	9	–	–	–
GKHB	–	–	–	1	2	7	4	3	9	2	–	–
NXHB	–	–	–	–	–	–	–	–	–	–	–	–
WCJK	–	–	–	–	3	4	1	1	5	–	–	–
CCX	–	–	–	–	–	3	2	2	4	3	–	–
LYHB	–	–	–	–	–	–	–	–	–	–	–	–

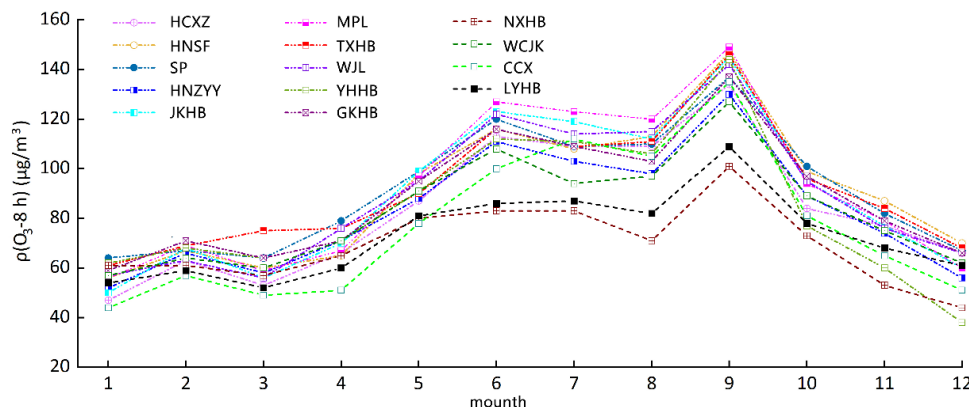


Figure 5. Variations in O_3 -8 h values in the monitoring stations in Changsha in 2021 in different months

Figure 6 depicts the seasonal variation characteristics of O_3 -8 h values in the 14 environmental monitoring stations in Changsha in 2021. The seasonal concentration value in this study stood for the arithmetic mean concentration value of the daily average maximum 8-h dynamic O_3 concentration within a quarter. In 2021, the O_3 concentrations in the 14 monitoring stations in Changsha were higher in summer and autumn compared with spring and winter, and the maximum values occurred in summer, which were in the range of 79–123 $\mu\text{g}/\text{m}^3$. The low values in winter were in the range of 50–66 $\mu\text{g}/\text{m}^3$. The O_3 concentrations were in the order of summer > autumn > spring > winter. Similarly, the seasonal variations in O_3 concentrations were more obvious in the national control stations than in the provincial control stations. The O_3 concentration reached a maximum of 123 $\mu\text{g}/\text{m}^3$ in the National Control Station, Mapoling, while it reached a maximum of 104 $\mu\text{g}/\text{m}^3$ in Hunan University of Chinese Medicine. The difference was 19 $\mu\text{g}/\text{m}^3$. The O_3 concentrations in the provincial control stations in the summer were ranked in the following order: Ningxiang Environmental Protection Bureau (106 $\mu\text{g}/\text{m}^3$) > Changsha County Government (100 $\mu\text{g}/\text{m}^3$) > Wangcheng District Economic Development Zone Management Committee (85 $\mu\text{g}/\text{m}^3$) > Liuyang Environmental Protection Bureau (79 $\mu\text{g}/\text{m}^3$). Generally speaking, the monthly and seasonal variation trends of O_3 were similar to those of most other cities, which were principally consistent with the analysis results of monthly and seasonal changes of O_3 concentrations in Zhengzhou and Chenzhou observed by Liu et al. (2022) and Zhou et al. (2022). In this study, the O_3 -8 h values showed opposite seasonal variation trends compared with $\text{PM}_{2.5}$, PM_{10} , and NO_2 possibly because the boundary layer was higher in summer and autumn, promoting the downward transport of O_3 from the stratosphere to the near-ground space (Mao et al., 2020).

Relationship between O_3 and the precursor NO_2 in each monitoring station in Changsha

According to the analysis results earlier, various factors, such as solar radiation, terrain, and primary emissions, controlled and affected the O_3 concentrations in the monitoring stations. Similarly, the precursors (NO_2 , VOCs, and so on) were also important influencing factors. The daily variations in O_3 and NO_2 concentrations in the 14 monitoring stations in Changsha in 2021 are illustrated in Figure 7. The NO_2 concentrations in all the stations fluctuated. The NO_2 concentrations commenced to rise in the early morning, which was the early rush hour. The increase in automobile exhaust emissions of urban vehicles was an important reason for the elevated NO_2 concentrations.

From 9:00 to 17:00, the quantity of NO₂ emissions reduced. The surface temperature continued to rise and the solar radiation continued to strengthen when NO₂ was continuously consumed to generate O₃. After 19:00, the NO₂ concentration commenced to gradually increase and reached its maximum at around 10:00. This trend continued until the next early morning. Then, the concentration declined gradually. After 17:00, solar radiation barely existed, and late rush hour took place in the city. In addition, the evening activities, such as barbecues and night snacks, were launched due to the rich and colorful night activities in Changsha, being the provincial capital city of Human province. The NO₂ concentration commenced to rise again, which was due to urban transportation, meteorological conditions, and emission sources (Fu et al., 2021). Obviously, the O₃ and NO₂ concentrations show opposite variation trends in this figure. The O₃ concentration exhibited a typical “inverted U-shaped” profile, whereas that of NO₂ principally showed a “U-shaped” profile. The variations in NO₂ concentrations were more evident in the national control stations than in the provincial control stations. Therefore, the relationship between O₃ concentration and the concentration of precursor NO₂ was analyzed from the perspective of principles of variations of photochemical reactions (Wang et al., 2017). The O₃ in the Earth’s atmosphere is finally generated from the combination reaction of atomic oxygen (O₃P) and molecular oxygen (O₂), and the O₃P is principally generated from the photolysis of NO₂ in the troposphere, promoting the formation of O₃. Once O₃ is formed, it easily reacts with NO to generate NO₂ again. If other chemicals are not involved, recycling reactions occur. However, the troposphere contains other oxidants, especially free radicals (HO₂ and RO₂), which can effectively convert NO into NO₂, leading to the accumulation of O₃. An effective “NO_x cycle” is established in the entire reaction process, and O₃ is generated without the consumption of NO_x. The entire reaction process of O₃ is extremely complex. If the NO level is high, usually in polluted urban areas, the production of O₃ is inhibited, and the “NO_x titration state” takes place (Tan et al., 2019). Although the quantity of NO_x emissions continues to decrease, the research results based on observations and emissions suggest that certain locations in the major urban areas in China may still be in the state of VOC–NO_x combustion emissions or O₃ generation restricted by NO_x during certain periods (Tan et al., 2018). Obtaining other precursors was difficult in this study, and the contributions of photochemical interactions of various precursors to the generation of O₃ should be analyzed in the future. This study emphasized that reducing O₃ pollution via concerted control of VOC–NO_x was necessary.

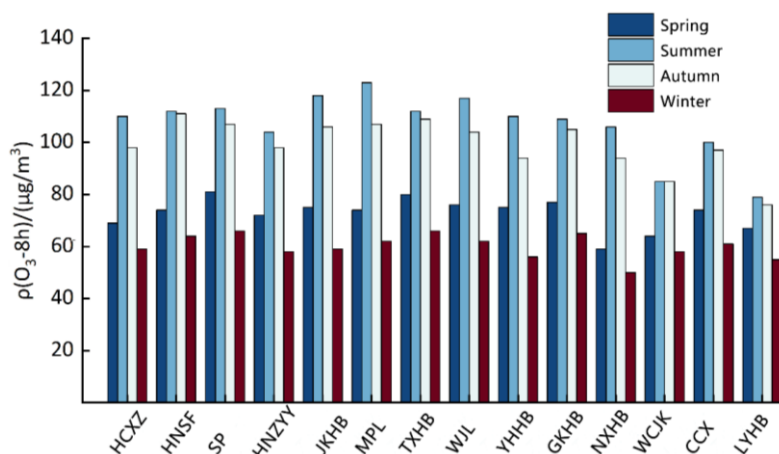


Figure 6. Variations in O₃–8 h values in the monitoring stations in Changsha in 2021 in different seasons

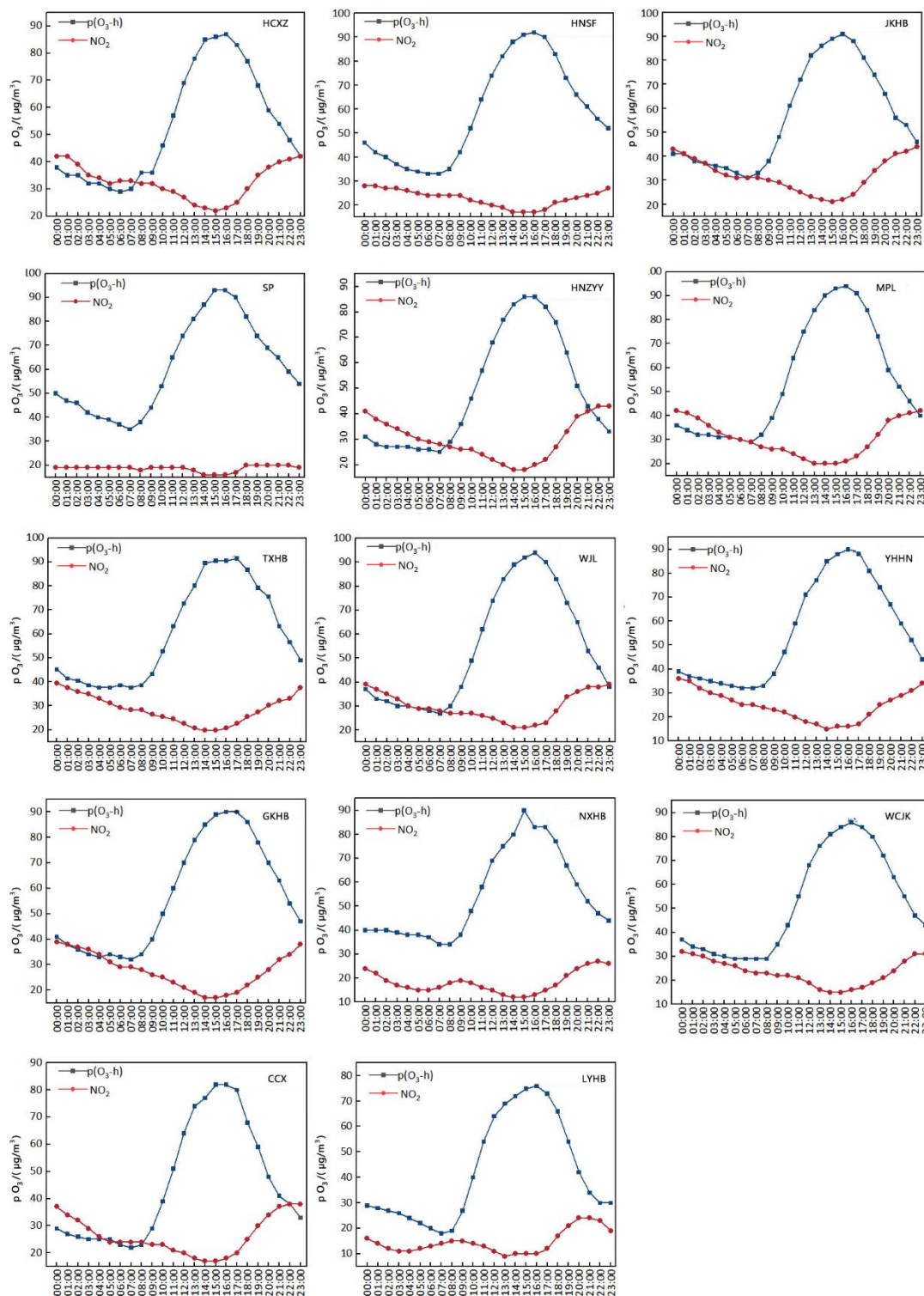


Figure 7. Daily variations in O_3 and NO_2 concentrations in the monitoring stations in Changsha in 2021

Analysis of the relationship between O_3 –8 h and meteorological factors

Studies reported that an increase in O_3 concentration at a city scale was related to artificial sources (industrial emissions, automobile exhaust, solvent application, biomass

combustion, fuel evaporation, and so on), emissions from biological sources (plant), as well as atmospheric transport capacity, dry and wet deposition of gases and aerosols, chemical reactions, and natural emission rates determined by meteorological conditions (Mozaffar et al., 2021). Wu et al. (2017) reported that the high-temperature and low-humidity conditions were favorable to the occurrence of O₃ pollution events in Chengdu. Deng et al. (2021) analyzed the relationship between O₃ concentration in Wuyishan City and meteorological conditions and reported that the O₃ concentration was significantly positively correlated with ultraviolet radiation and atmospheric temperature. At a wind speed of ≤ 2.0 m/s, the frequency of excessive O₃-8 h values also increased. Bai et al. (2022) analyzed the average mass concentration of O₃-8 h in Tianjin and found that the concentration of O₃ was relatively high under the conditions of daily maximum temperature >30°C, RH of 20%–70%, southwest or southeast wind speed of 1–2.5 m/s, and daytime boundary-layer height < 1400 m. Based on these studies, this study preliminarily explored the relationship between the O₃ concentration and meteorological factors in the environmental monitoring stations in Changsha. The correlations between O₃-8 h and wind speed, wind direction, atmospheric pressure, atmospheric temperature, and humidity are shown in *Figure 8*. The correlation coefficients between O₃ concentration and meteorological factors were not consistent. The O₃ concentration was significantly positively correlated with daily average wind speed and atmospheric temperature and extremely correlated with atmospheric temperature, with a correlation coefficient of 0.65. The O₃-8 h value was negatively correlated with the wind direction, atmospheric pressure, and humidity and significantly negatively correlated with the wind direction and RH. The correlation coefficient between O₃-8 h value and RH was as low as -0.48. Therefore, the impact of temperature, humidity, and wind speed on O₃-8 h in Changsha was analyzed. The national control monitoring station Environmental Protection Bureau in the Tianxin District and the provincial control monitoring station Environmental Protection Bureau in Liuyang City were selected because one was located in the urban area and the other in the suburb. The difference between the two stations was obvious, and hence the contrast was strong. The meteorological data of the two stations was intact without missing values.

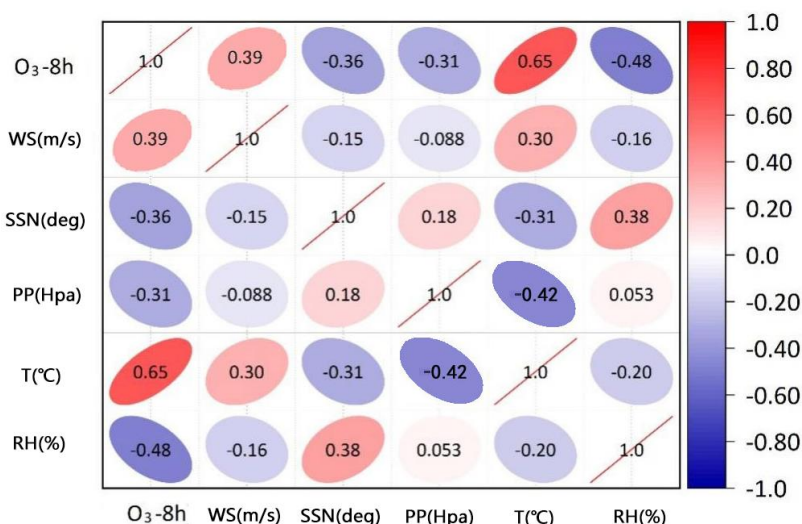


Figure 8. Correlations between O₃-8 h value and meteorological factors. WS-Wind speed; SSN-wind direction; PP-atmospheric pressure; T-atmospheric temperature, and RH-humidity

Analysis of the relationships between O₃-8 h and atmospheric temperature, humidity, and wind speed

The O₃-8 h value gradually increased with the increase in temperature (*T*). At *T* < 10°C, the O₃ concentration reached a minimum of only 52 µg/m³, and the ratio of pollution days based on O₃-8 h was 0 (Table 4). At 10 < *T* < 20°C, the O₃ concentration was still low. At *T* > 30°C, the O₃-8 h value increased from 71 to 116 µg/m³, an increase of 45 µg/m³. The ratio of pollution days reached 12.9%. However, the RH had the opposite effect on the O₃-8 h value compared with the atmospheric temperature. The higher the RH, the lower the O₃-8 h value. Under the condition of RH > 90%, the O₃ concentration was merely 49 µg/m³. Moreover, under the condition of RH > 70%, the ratio of pollution days based on O₃-8 h was 0. Under the condition of 50% < RH ≤ 70%, the O₃-8 h value was 98 µg/m³, with a low ratio of pollution days of only 3.4%. Under the condition of RH ≤ 50%, the O₃ concentration increased from a minimum of 49 µg/m³ to 109 µg/m³, an increase of 60 µg/m³. The ratio of pollution days based on O₃-8 h reached 14.2%. The effects of wind speed and RH on the O₃-8 h value were similar. Namely, the increase in the wind speed inhibited the generation of O₃, while a low wind speed promoted the generation of O₃-8 h, indicating that the conditions of high temperature, low humidity, and low wind speed contributed to the pollution due to concentrated O₃. In detail, the conditions of an atmospheric temperature of around 30°C, RH of around 50%, and wind speed of 0.5–2 m/s were favorable to the generation of O₃ in Changsha.

Table 4. Relationships between the daily average atmospheric temperature, wind speed, humidity, and O₃-8 h in the monitoring stations in Changsha in 2021

Daily average atmospheric temperature (<i>T</i> /°C)	O ₃ -8 h (µg·m ⁻³)	Ratio of pollution days based on O ₃ -8 h/%	Daily average relative humidity (RH/%)	O ₃ -8 h (µg·m ⁻³)	Ratio of pollution days based on O ₃ -8 h/%	Daily average wind speed (F/m/s)	O ₃ -8 h (µg·m ⁻³)	Ratio of pollution days based on O ₃ -8 h/%
<i>T</i> ≤ 10	52	0	RH ≤ 50	109	14.2%	F ≤ 1	77	1.4%
10 < <i>T</i> ≤ 20	71	1%	50 < RH ≤ 70	98	3.4%	1 < F ≤ 2	89	3.2%
20 < <i>T</i> ≤ 30	95	2.4%	70 < RH ≤ 90	74	0	2 < F ≤ 3	88	4.1%
<i>T</i> > 30	116	12.9%	RH > 90	49	0	F > 3	0	0

The scatter plots and fit results of the O₃-8 h values, atmospheric temperature, RH, and wind speed are shown in Figure 9. The O₃-8 h values were positively correlated with the temperature and wind speed while negatively correlated with the RH. The O₃-8 h values obviously increased with the increase in temperature. The daily maximum temperature was directly related to the solar radiant intensity and radiation duration. At a higher temperature, the quantity of O₃ produced by the photochemical reactions increased. The fit results of O₃-8 h against RH showed that the fit was good if the RH of the urban region was in the range of 40%–80% or the RH of the suburb was in the range of 60%–80%. The increase in humidity would reduce the quantity of O₃ generated. However, the fit was good if the wind speed in the urban stations was in the range of 0.5–2.0 m/s, or the wind speed in the suburban stations was in the range of 0.5–1.5 m/s. These findings, together with the conclusions from various studies, disclosed the importance of meteorological factors in determining the interannual variation in O₃ concentration in summer. In addition, meteorological factors are also crucial in evaluating the effectiveness of emission control measures. The meteorological conditions such as temperature and humidity alter the distribution efficiency of chemical reactions and dry

deposition, thus regulating the production and loss of O₃ (Wang et al., 2020). Previous studies have shown that the concentrated O₃ is usually formed under the conditions of long sunshine hours, low wind speed, and low RH, which are favorable to the photochemical reactions of O₃ and the accumulation of O₃ precursors. The wind direction is also essential because it can affect the transportation of pollutants, thereby forming concentrated O₃ in the wind direction (Huang et al., 2019). Therefore, the meteorological and environmental departments should focus on the crucial impact of meteorological factors on the short-term changes in O₃ concentration.

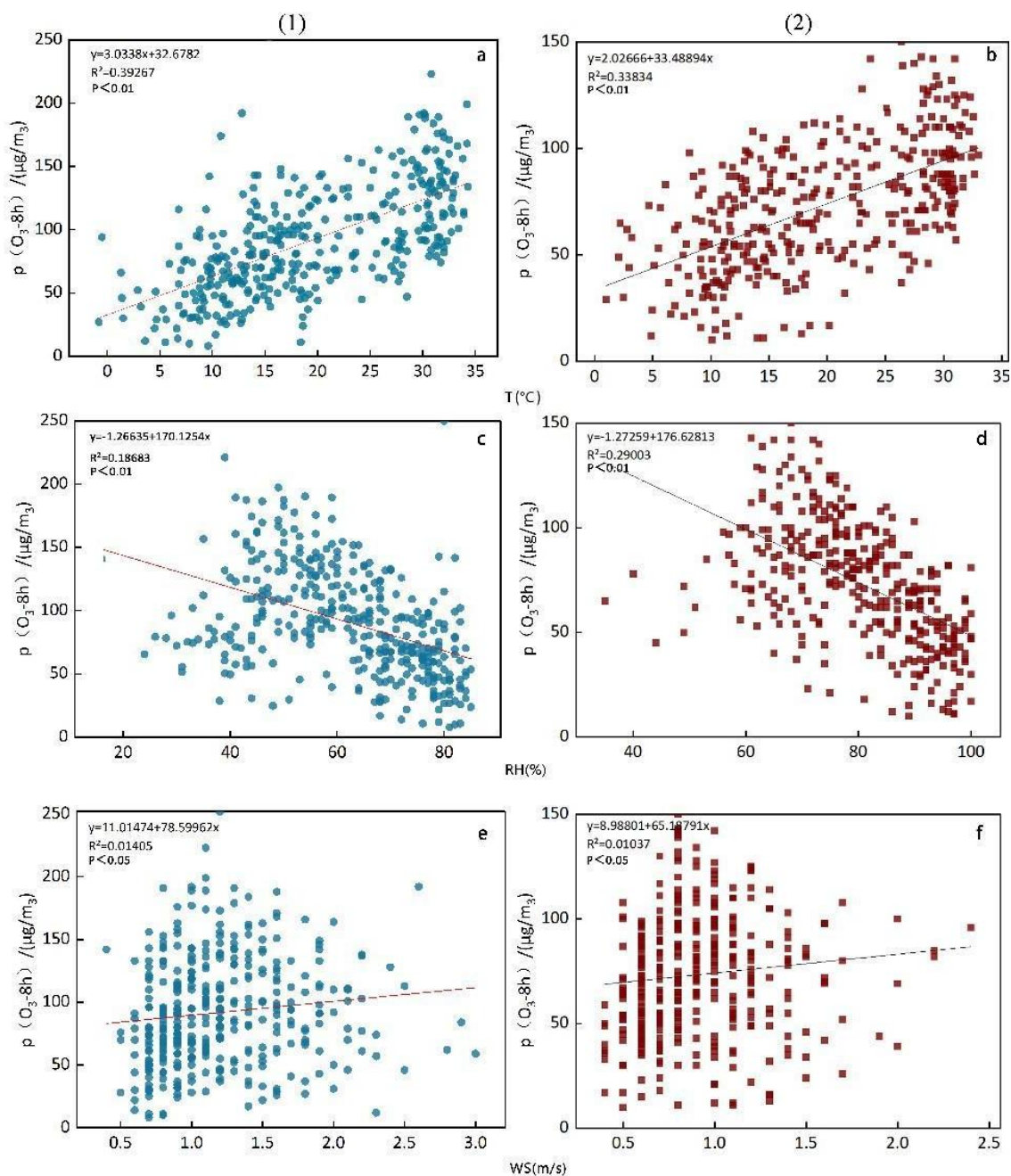


Figure 9. Scatter plots and fit results of the O₃ concentrations and meteorological factors. (1) Environmental Protection Bureau in the Tianxin District, and (2) Environmental Protection Bureau in the Liuyang City. T-Atmospheric temperature; RH-Relative humidity; WS-Wind speed

Discussion

During 2021, the air quality of 14 environmental monitoring stations in Changsha was less affected by sulfur dioxide, nitrogen dioxide (NO₂), and carbon monoxide. Particulate matter and O₃ were the main factors affecting air quality. Analysis revealed that the increasing trend of ozone concentration in Changsha was primarily attributed to the rapid rise in emissions of ozone precursors such as volatile organic compounds (VOCs) and nitrogen oxides (NO_x). Overall, industrial emissions and traffic exhaust were the main contributors to this issue. Changsha's numerous factories and enterprises had a noticeable impact on air quality due to their emissions of waste gas and particulate matter. Furthermore, the substantial increase in the city's car population has led to motor vehicle exhaust emissions becoming a significant factor in air pollution, exacerbating the air quality problem.

In addition, the short-term impact of seasonal meteorological effects on ozone concentration varied greatly. Changsha is located in the subtropical monsoon climate zone, which is conducive to the formation of ozone, leading to ozone-induced pollution events and further aggravating air pollution problems. At the same time, previous studies had shown that high temperature and low humidity were favorable meteorological conditions for photochemical reaction and ozone generation (Shen et al., 2015; Zhao et al., 2016). The results of this study also further proved that the influence of temperature and humidity on ozone concentration was relatively stable on the scale of diurnal variation and step change, and other meteorological factors (such as wind speed and air pressure) also had a great influence on ozone concentration. Chen et al. (2019) showed that the one-way influence mechanism of meteorology on ozone concentration in Beijing was relatively simple. In summer, high temperatures and low humidity were shown to be favorable conditions for ozone production, which is usually considered to be the main reason for the highest ozone concentration in summer. The results of this study also showed that the summer ozone concentration in Changsha was relatively less affected by meteorological factors. Therefore, the rapid increase of ozone precursors such as VOCs and NO_x in summer was the main reason for the increase of ozone concentration. VOCs and NO_x were mainly anthropogenic and natural source emissions (Dentener et al., 2006; Feng et al., 2018). Wang et al. (2018) used remote sensing images to monitor long-term biogenic emissions and found that warming had led to a significant increase in biogenic emissions in Beijing in recent years. Therefore, climate warming may be a major driving factor for the increase of ozone pollution events in China. At present, a large number of scholars have found that the use of meteorological means such as artificial rainfall and high-rise building sprinklers (Yu, 2014) reduced short-term ozone pollution and alleviated urban heat islands.

However, compared with other first-tier cities (such as Beijing, Shanghai, and Guangzhou), Changsha's air pollution level had its unique characteristics compared with other large cities and regions. Changsha's air pollution level was at an upper-middle level in the country. Compared with other small and medium-sized cities, Changsha had higher industrial activities and traffic density, resulting in larger emissions of pollutants such as particulate matter and ozone. This situation made Changsha face more complex challenges in improving air quality. To this end, the government needed to strengthen the management and supervision of industrial enterprises' emissions, ensure that their emissions met national standards, and encourage enterprises to promote cleaner production technologies. In the meanwhile, established a sound monitoring system, regularly release emission data and

environmental quality status, and promote enterprises to fulfill their environmental responsibilities. Furthermore, the construction of convenient bicycle lanes and walking systems to encourage non-motorized travel to reduce motor vehicle exhaust emissions, as well as the strengthening of the management and protection of green space to ensure it continued to play the role of purifying air, were potential solutions to reduce ozone pollution events.

Conclusions

The following conclusions were drawn from this study:

(a) SO₂, NO₂, and CO had little effect on air quality, while O₃ and particulate matter exceeded the standard pollution days significantly more than in suburban sites.

(b) The monthly and daily average concentrations and seasonal variations of O₃ concentration were different at different sites. The O₃ concentration in urban sites was significantly higher than that in suburbs.

(c) The concentration of O₃ and NO₂ showed an opposite trend. At the same time, under the influence of meteorological factors, the formation of O₃ in Changsha was promoted under certain conditions (about 30°C atmospheric temperature, about 50% relative humidity, and 0.5-2 m/s wind speed).

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