



Article Factors Influencing O₃ Concentration in Traffic and Urban Environments: A Case Study of Guangzhou City

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Abstract: Ozone (O₃) pollution is a serious issue in China, posing a significant threat to people's health. Traffic emissions are the main pollutant source in urban areas. NO_X and volatile organic compounds (VOCs) from traffic emissions are the main precursors of O₃. Thus, it is crucial to investigate the relationship between traffic conditions and O₃ pollution. This study focused on the potential relationship between O₃ concentration and traffic conditions at a roadside and urban background in Guangzhou, one of the largest cities in China. The results demonstrated that no significant difference in the O₃ concentration was observed between roadside and urban background environments. However, the O₃ concentration was 2 to 3 times higher on sunny days (above 90 μ g/m³) than on cloudy days due to meteorological conditions. The results confirmed that limiting traffic emissions may increase O₃ concentrations in Guangzhou. Therefore, the focus should be on industrial, energy, and transportation emission mitigation and the influence of meteorological conditions to minimize O₃ pollution. The results in this study provide some theoretical basis for mitigation emission policies in China.

Keywords: ozone; nitrogen dioxide; traffic condition; impact factors

1. Introduction

Air pollution has become a crucial issue in China due to rapid economic development [1]. The Chinese government has exerted a significant effort to reduce air pollution in recent years. As a result, fine particulate matter ($PM_{2.5}$) has significantly decreased due to strict emission mitigation policies [2]. Ozone (O₃) has become the most prevalent pollutant in China. The O₃ concentration has increased by 10.6% from 2015 to 2021 in 339 [3,4]. Excessive exposure to O₃ can be extremely harmful to human health, causing substantial damage and irritation to the eyes, respiratory tract, and lungs [5–7].

Many studies have focused on O_3 pollution in China, investigating the spatiotemporal variations [8–12], secondary formation mechanism [13–15], emission sources [16–19], and other factors. The Pearl River Delta (PRD) is one of the most developed regions in China and has experienced significant O_3 pollution. The O_3 concentration has increased in the PRD since 2015 [20]. The O_3 pollution is the highest in autumn in the PRD due to high temperatures, strong solar radiation, and low relative humidity (RH) [21–25]. In addition, several studies confirmed the "weekend effect" [26,27] in China, i.e., the O_3 concentration is higher on weekends than during working days in Beijing [28], Shanghai [29,30], and Guangzhou [31]. There are two reasons. First, the nitric oxide (NO) concentration is lower during the weekend due to fewer traffic emissions. Therefore, the inhibitory effect of NO on O_3 is weaker, and more O_3 is generated. Second, fewer aerosol particles are emitted



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Copyright: © 2022 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). during the weekend, resulting in less scattering and absorption of solar radiation. As a result, more O_3 is formed due to the stronger solar radiation during weekends [32].

There are three major sources of near-ground O₃ precursors: traffic emissions [33], industry emissions, and emissions by power plants [34]. Mitigating O₃ pollution has become a crucial issue in the PRD region in recent years [35]. However, it is challenging to control O₃ pollution due to the complex O₃ generation mechanism [36]. After absorbing ultraviolet light, tropospheric O₂ decomposes into two O atoms. The O atoms are combined with O₂ to form O₃ (Equations (1) and (2)). In urban areas, NO₂ in traffic emissions is the main precursor of O₃ (Equation (3)). O₃ rapidly oxidize NO to form NO₂, known as the titration effect (Equation (4)).

$$O_2 + UV \to O + O \tag{1}$$

$$O + O_2 + M \rightarrow O_3 + M \tag{2}$$

$$NO_2 + hv \rightarrow NO + O$$
 (3)

$$O_3 + NO \rightarrow NO_2 + O_2 \tag{4}$$

In these processes, a dynamic equilibrium exists during the formation and consumption of O_3 by NO_X . However, alkoxy radicals (RO) and hydroperoxyl radicals (HO₂) generated by the reaction of volatile organic compounds (VOCs) and hydroxyl (OH) radicals in the atmosphere also react with NO (Equations (5)–(8)), destroying the dynamic balance between NO_X and O_3 and increasing the O_3 concentration.

$$HO_2 + NO \rightarrow HO + NO_2$$
 (5)

$$RO_2 + NO \rightarrow RO + NO_2$$
 (6)

$$HO + RH + O_2 \rightarrow RO_2 + H_2O \tag{7}$$

$$RO + O_2 + hv \rightarrow HO_2 + RCHO$$
 (8)

If large amounts of NO_X are emitted, HO and RO₂ react predominantly with NO₂ (Equations (9) and (10)); if small amounts of NO_X are emitted, the free radical reaction dominates (Equations (11) and (12)). According to the formation mechanism of O₃, the O₃ concentration is closely related to the NO_X and VOCs concentrations because of the highly nonlinear relationship between O₃ and its precursors. Therefore, it is more difficult to mitigate O₃ than other pollutants.

$$RO_2 + NO_2 \rightarrow RO_2NO_2$$
 (9)

$$HO + NO_2 \rightarrow HNO_3$$
 (10)

$$HO_2 + HO_2 \rightarrow H_2O_2 + O_2 \tag{11}$$

$$HO_2 + RO_2 \rightarrow RO_2H + O_2 \tag{12}$$

The O₃ concentration depends on the O₃ formation process and diffusion [37–39]. Accordingly, the photochemical reaction rate [40], human activities, and meteorological conditions are the three dominant factors affecting the local O₃ concentration [41,42]. Many studies have demonstrated that low cloudiness [43,44], intense solar radiation [45], high temperature [46,47], and low RH [48] can accelerate the O₃ production rate [49,50]. High road network density [51], frequent motor vehicle braking, rapid acceleration, and high traffic flow [52] lead to high NO_X emissions [53]. Wind speed and direction can affect the horizontal distribution of O₃ in local areas, and a low wind speed facilitates O₃ accumulation [54,55].

Traffic emissions are the main pollutant source in urban areas. NO_X and VOC from traffic emissions are the main precursors of O_3 . Therefore, it is necessary to investigate the relationship between traffic conditions and O_3 pollution. However, there are very few studies focusing on the influence of traffic situations on O_3 . We investigate the potential

relationship between the O_3 concentration and traffic conditions at roadside and urban background stations in Guangzhou, one of the largest cities in the PRD and China. The results provide a scientific reference for policymakers to establish emission mitigation policies.

2. Materials and Methods

2.1. Study Area and Measurement Data

Guangzhou is one of the largest cities in China, with a developed economy, dense population, and advanced manufacturing industries. The atmospheric pollutant concentrations were obtained from three national monitoring stations: two roadside stations (Yangji station (YJ station) and Huangsha station (HS station)) and one urban background station (Luhu station (LH station)) (Figure 1). The YJ station is located at an intersection of the main road (Zhongshan road) in the city center, about 5 m higher above ground. The HS station is located on a three-layer viaduct. The measurement instruments were installed between the second and third layers, about 20 m above the ground. The LH station is situated in Luhu Park, allowing us to compare air pollution in traffic and an urban park. The national measurement data were obtained from Guangzhou Ecological Environment Bureau (http://sthjj.gz.gov.cn/, accessed on 1 July 2021). The temporal resolution of the measurement data is one hour.

Meteorological data were obtained from Guangzhou Weather website (http://www. tqyb.com.cn/gz/weatherLive/autoStation/, accessed on 1 July 2021), including ambient temperature, wind speed, wind direction, solar radiation, and RH. The dynamic traffic data were obtained from the Guangzhou Municipal Bureau of Transportation (http://jtj.gz.gov. cn/jtcx/lkcx/, accessed on 1 July 2021). All the data were quality-controlled and covered the period from January to June 2021.

2.2. Analysis Approaches

A stepwise regression model was used to investigate the relationship between the potential impact factors and O_3 concentration. Stepwise regression analysis automatically selects the most important variables to establish a predictive or explanatory model. The influencing factor are incorporated into the model one by one, and the statistical significance was evaluated. The insignificant factors were removed from the model.



Figure 1. Cont.



Figure 1. Overview of the study area and atmospheric monitoring stations. (**a**) Location of three stations; (**b**) Luhu station (LH); (**c**) Huangsha station (HS); (**d**) Yangji station (YJ).

3. Results and Discussion

3.1. Temporal Variations of NO₂ and O₃

3.1.1. Daily Variations

Generally, pollutant concentrations are affected by several factors, such as emission sources, meteorological conditions, and pollutant formation mechanisms. The median diurnal variation of O_3 and NO_2 during the cold (from January to March) and warm (from April to June) seasons is shown in Figure 2. Similar diurnal patterns of O_3 are observed at the three stations. The O_3 concentration is low from 22:00 to the early morning on the following day. Then, it rapidly increases from around 8:00 in the morning and reaches the maximum around 14:00–16:00. As the solar radiation increases during the daytime, the O_3 concentration increases [56,57] (Equations (1) and (2)). However, the O_3 concentration remains low during the night. There are two reasons. First, less O_3 is generated in the absence of sunlight. Second, NO can react with O_3 to form NO_2 and O_2 during the night (Equation (4)), which is referred to as the titration effect of NO.

The diurnal variation of NO₂ differs from that of O₃. As shown in Figure 2d–f, the NO₂ concentration is lower at 3:00–4:00 and 12:00–16:00 and higher at 6:00–8:00 and 20:00–22:00. The highest NO₂ concentration occurs at 20:00–22:00. The NO₂ concentration shows an increasing trend from 04:00–8:00 at the two roadside stations (HS and JY) because of traffic emissions. This increasing trend is not observed at the urban background station (LH). The solar radiation increases after 08:00. NO₂ reacts with VOCs to produce O₃, resulting in a decreasing trend at all three stations. The NO₂ concentration increases after 16:00 due to lower solar radiation and a decrease in the photochemical reaction [58–60]. During the night, the NO₂ concentration increases again due to the titration effect [61].

The seasonal difference in the pollutant concentration is larger for NO_2 than for O_3 , as shown in Figure 2d–f. The NO_2 concentration is higher in the cold season (from January to March) than in the warm season (from April to June). The decisive factor influencing the seasonal variation of the NO_2 concentration is solar radiation. The average solar radiance in Guangzhou is 1352 kJ/ m² in the cold season and 1806 kJ/ m² in the warm season. Lower solar radiation leads to less O_3 generation and less NO_2 consumption. Another possible factor may be the lower RH in winter. In Guangzhou, the average RH is 59.04% and 86.2% in the cold and warm seasons, respectively [62,63]. A higher RH results in

a stronger photochemical reaction and a lower NO_2 concentration in the warm season. Another possible explanation is the seasonal change in the planetary boundary layer height. It is 717 m in winter and 1239 m in summer in Guangzhou [64,65]. A lower planetary boundary layer accumulates NO_2 , resulting in a higher NO_2 concentration [66]. However, the seasonal difference in the O_3 concentration is smaller than that of the NO_2 concentration. The reason is that O_3 is a secondary pollutant whose concentration is controlled by highly complex and nonlinear secondary formation mechanisms.



Figure 2. Diurnal variation of typical pollutants in cold and warm seasons: O₃ concentrations at (a) HS station, (b) YJ station, and (c) LH station; NO₂ concentrations at (d) HS station, (e) YJ station, and (f) LH station.

3.1.2. Weekly Variations

The weekly variations in the O_3 and NO_2 concentrations at the three stations are illustrated in Figure 3. In general, the weekly trends of the O_3 and NO_2 concentrations are similar at three stations, but the average concentrations are different. As shown in Figure 3a, the O_3 concentration is significantly higher on weekends (Saturday and Sunday) than on weekdays (from Monday to Friday), indicating the weekend effect of O_3 . It is believed to be related to a change in the proportion of O_3 precursor emissions and other pollutant emissions from human activities [67]. Fewer human activities on weekends lead to lower $PM_{2.5}$ and a lower aerosol optical thickness and radiation extinction. Therefore, the O_3 concentrations are higher on the weekend than on weekdays due to stronger photochemical reactions [68,69]. Moreover, high traffic flow during the morning rush hour results in a rapid increase in the NO concentration, inhibiting O_3 formation on weekdays [70,71].

Differences in the O_3 concentration are observed at the three stations. The highest O_3 concentration was measured at the LH station, followed by the two roadside stations YJ and HS. The reason is the surrounding environment. The LH station is located in Luhu Park. VOCs generated by biological sources compete with NO, reducing the inhibition of NO on O_3 and leading to a higher O_3 concentration [72,73]. The YJ station is surrounded mostly by business and entertainment areas with frequent human activities. Large amounts of NO_X are emitted from traffic inhibited O_3 formation. In addition, the titration effect of NO is stronger at the YJ station, leading to a slightly lower O_3 concentration at the YJ station than at the LH station. The HS station is a roadside station located near a park. It has higher vegetation cover than the YJ station.

The weekly variation in the NO₂ concentration shows a significantly different pattern than that of the O_3 concentration. The NO₂ concentration is slightly higher on weekdays than on the weekend due to higher anthropogenic emissions, especially traffic emissions in urban areas [74–77]. The NO₂ concentration is the highest at the HS station, followed by the



YJ and LH stations, which is consistent with the traffic emissions and the local environment of the three stations.

Figure 3. Weekly variation in O₃ (a) and NO₂ (b) concentrations at the three stations.

3.2. Influencing Factors

3.2.1. Synergistic Variation of O₃ and NO₂

Figure 4 shows the scatterplots of the O_3 and NO_2 concentrations during the daytime (07:00–19:00) and nighttime (20:00–06:00) at the three stations. The linear regression model has a negative slope for all three stations during the daytime and nighttime, indicating that the NO₂ concentration decreases as the O_3 concentration increases. However, differences are observed between daytime and nighttime. In the daytime, NO₂ is consumed, and O_3 is produced (Equations (2) and (3)). However, without a photochemical reaction during nighttime, O_3 is converted to NO₂ due to the titration effect (Equation (4)), leading to a lower O_3 concentration. Due to the highly nonlinear and complex O_3 formation mechanism, the R² value is low for all fitting results. The R² value is larger during nighttime at all three stations due to the absence of the photochemical reaction, the titration effect of NO, and weaker vertical diffusion [78,79]. The nighttime fitting degree is better at the LH station than at the roadside stations. The reason might be the surrounding environment of the LH station. The vegetation cover is higher; thus, vegetation respiration is stronger at night. Consequently, the NO₂ and O₃ concentrations are relatively stable, leading to a better fitting degree.

The fitted results of the three stations are similar. However, the dominant emission sources differ at the three stations. This result indicates no significant effect of traffic emissions on the O_3 concentration at the roadside stations. Due to the absence of VOCs, a dynamic equilibrium exists between O_3 and NO_X in the atmosphere. Thus, O_3 is not accumulated and does not exceed the air pollution standard [80,81]. However, the reaction between VOCs and NO weakens the inhibitory effect of NO on O_3 , resulting in high O_3 pollution [82]. Controlling NO_X emissions does not mitigate O_3 pollution. Moreover, Guangzhou is in the VOC-limitation area [83,84]. Limiting vehicle emissions to reduce the NO_X concentration may even increase the O_3 concentration. Therefore, the focus should be on industrial, energy, and transportation emission mitigation and the influence of meteorological conditions to minimize O_3 pollution.



Figure 4. Scatterplot of O₃ and NO₂ concentrations at HS (a), YJ (b), and LH (c).

3.2.2. Pearson Correlation and Stepwise Regression Analyses

Pearson correlation analysis and stepwise regression analysis were conducted to describe the relationship between the pollutant concentration and other factors, such as meteorological parameters and dynamic traffic parameters. Tables 1 and 2 show the results of Pearson's correlation analysis and stepwise regression analysis, respectively. Pearson's correlation shows the correlation between the O₃ concentration and potential factors, and the stepwise regression model determines the significant impact factors. The beta values are used to quantify the contribution of the variables. Briefly, the O₃ concentration is positively correlated with solar radiation, temperature, and travel-time ratio and negatively correlated with the NO₂ concentration, wind speed, and vehicle speed (Table 1). The stepwise regression model shows that the significant factors affecting O₃ concentration are temperature, NO₂ concentration, and RH. As shown in Table 1, the O₃ concentration

positively correlates with the travel-time ratio. The travel time ratio is the ratio of the actual travel time to the ideal travel time in smooth traffic flow. The larger the ratio, the higher the degree of traffic congestion. The NO_X and VOC emissions are higher during frequent vehicle braking than during uniform driving. Thus, more O_3 precursors are emitted, leading to a significant positive correlation between O_3 concentration and travel-time ratio. The temperature is positively correlated with O_3 concentration as a result of O_3 formation. The negative correlation between the NO₂ and O_3 concentrations has already been discussed in Section 3.2.1. Moreover, a negative correlation is observed between vehicle speed and O_3 concentration. The fuel consumption is higher at higher speeds than at lower speeds, resulting in more precursor emissions and a higher O_3 concentration. Wind speed and O_3 concentration are negatively correlated because of the dilution effect. The O_3 concentration is lower at higher RH due to wet deposition. Moreover, an increase in RH significantly reduces the number of oxygen atoms, reducing the amount of O_3 generation.

Tabl	e 1.	Pearson	's correlation	coefficients	between (Oʻ	3 concentration and	d various i	factors.
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Impact Factors	Daytime	Nighttime		
Temperature (°C)	0.047 **	0.057 **		
Wind speed (m/s)	-0.082 **	-0.057 **		
Daily precipitation (mm)	-0.101 **	-0.006		
Vehicle speed (m/s)	-0.111 **	-0.111 **		
Travel-time ratio	0.150 **	0.129 **		
NO ₂ ($\mu g/m^3$)	-0.220 *	-0.153 **		
RH (%)	-0.495 **	-0.226 **		
Solar radiation (J/m ²)	0.448 **	0.279 **		

* Significant at the 0.01 level. * Significant at the 0.05 level.

Table 2. Results of stepwise regression model between O₃ concentration and various factors.

M- J-1	Daytime	11	Nighttime	p	
widdel	Beta Value	P	Beta Value		
Temperature (°C)	0.386	0.000	0.207	0.000	
Wind speed (m/s)	-0.076	0.000	-0.124	0.000	
Daily precipitation (mm)	0.092	0.000	0.036	0.037	
Vehicle speed (m/s)	-0.077	0.000	-0.063	0.000	
$NO_2 (\mu g/m^3)$	-0.407	0.000	-0.611	0.000	
RH (%)	-0.578	0.000	-0.389	0.000	
Solar radiation (J/m ²)	-	-	0.182	0.000	

The dependent variable: O_3 (µg/m³).

The secondary pollutant O_3 is correlated with several factors. The vehicle speed and travel-time ratio are significantly correlated with the O_3 concentration, indicating the importance of traffic emissions on O_3 pollution in urban areas.

3.2.3. Case Study

As discussed in the previous section, traffic emissions affect the O_3 concentration but are not the dominant factor. Many studies demonstrated that solar radiation was a significant factor influencing O_3 formation. A case study was conducted to quantify the influence of solar radiation on O_3 concentration in Guangzhou. Two weeks were selected: 1 February to 7 February 2021, with sunny weather, and 24 February to 2 March 2021, with cloudy weather.

The pollutant concentrations and related parameters are listed in Table 3. The O_3 concentration is substantially different on sunny and cloudy days at all three stations, indicating the predominant influence of solar radiation. The O_3 concentration is 2–3 times higher on sunny days than on cloudy days in the daytime and nighttime. However, there are no large differences in the NO₂ concentration. In the daytime, there are no differences in the NO₂ concentration between sunny and cloudy days. However, the nighttime NO₂

concentration is 1.5 to 2 times higher on sunny days than on cloudy days. More O_3 is formed during sunny days, leading to a stronger titration effect and a higher NO₂ concentration during the nighttime on sunny days. It should be noted that the NO₂ concentration is lower at the LH station than at the two roadside stations during the daytime. However, the O_3 concentration is similar at all three stations due to the lower inhibitory effect of NO, as discussed in Section 3.1.2. This finding confirms our results, i.e., traffic emissions contribute significantly to O_3 generation, but the contribution is not higher at roadside stations than at the urban background station.

		Ο ₃ (μg/m ³)		$NO_2 (\mu g/m^3)$		Travel-Time Ratio		Solar	
Period	Station	Day Time	Night Time	Day Time	Night Time	Day Time	Night Time	Radiation (KJ/m ²)	RH (%)
	HS	97.43	52.95	54.28	79.05	1.14	1.03		
Sunny days	JY	94.70	63.45	48.80	63.66	1.25	1.06	17,627.04	64.71%
	LH	102.31	45.88	38.87	79.34	-	-		
	HS	37.30	21.15	52.34	53.10	1.21	1.05		
Cloudy days	JY	42.90	27.86	46.16	48.26	1.29	1.08	10,300.89	75.08%
	LH	41.70	25.75	36.99	41.59	-	-		

Table 3. The pollutant concentrations and related parameters in the two periods.

The scatterplots of the NO₂ and O₃ concentrations in the two periods at YJ and HS are shown in Figure 5. The colored dots indicate the dynamic traffic conditions. The linear regression results demonstrate that the negative correlation between the NO₂ and O₃ concentrations is stronger during the daytime than during the nighttime at both stations due to the stronger photochemical reaction strength. Furthermore, no significant relationship is observed between the O₃ concentration and dynamic traffic conditions.



Figure 5. Scatterplot of daily O₃ and NO₂ concentrations in the two periods at the HS (**a**) and YJ (**b**) stations. The colored dots denote the travel-time ratio.

4. Conclusions

This study evaluated the factors influencing the O_3 concentration in traffic and urban background environments. The diurnal and weekly variation of the O_3 and NO_2 concentrations demonstrated a similar pattern at the three stations. These results were attributed to differences in the O_3 generation mechanism, meteorological conditions, and emission sources. However, no significant differences in the O_3 variation were observed between the three stations, implying that the O_3 concentration was not significantly higher in the traffic environment than in the urban background environment. Since Guangzhou is located in a VOC-limited area, the lower O_3 concentration in the urban background area is due to the lower inhibition of NO on O_3 .

Pearson correlation analysis and stepwise regression analysis were used to describe the relationship between the pollutant concentration and the influencing factors, such as meteorological and dynamic traffic parameters. Traffic and meteorological parameters (temperature, solar radiation, RH, and precipitation) were significantly correlated with the O_3 concentration at the two roadside stations. It was concluded that traffic emissions contributed to O_3 pollution in the urban area but were not the decisive factor, while the meteorological factors also influenced the O_3 concentration.

A case study was conducted for two weeks to quantify the influence of solar radiation on O_3 concentration in Guangzhou. On sunny days, the O_3 concentration exceeded 90 μ g/m³ at the three sites. It was 2 to 3 times higher than during cloudy days due to meteorological conditions. The dynamic traffic condition (travel-time ratio) had no significant relationship with the O_3 and NO_2 concentrations at the two roadside stations.

This study analyzed the temporal variation of O_3 and its precursor NO_2 at roadside and urban background environments in Guangzhou and its influencing factors. The results confirmed that limiting traffic emissions might increase O_3 concentrations in Guangzhou. Therefore, emission mitigation should be performed, i.e., industrial, energy, and transportation emission mitigation, and the influence of meteorological conditions should be considered to minimize O_3 pollution. However, some limitations exist in this study. Due to a lack of NO and VOCs data, the relationship between O_3 concentration and NO and VOCs was not analyzed. In future, a mobile measurement focusing on O_3 will be carried out in Guangzhou, and a more detailed analysis will be performed.

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