Factors Influencing O\textsubscript{3} Concentration in Traffic and Urban Environments: A Case Study of Guangzhou City

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Abstract: Ozone (O\textsubscript{3}) 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\textsubscript{x} and volatile organic compounds (VOCs) from traffic emissions are the main precursors of O\textsubscript{3}. Thus, it is crucial to investigate the relationship between traffic conditions and O\textsubscript{3} pollution. This study focused on the potential relationship between O\textsubscript{3} 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 O\textsubscript{3} concentration was observed between roadside and urban background environments. However, the O\textsubscript{3} concentration was 2 to 3 times higher on sunny days (above 90 \(\mu\)g/m\(^3\)) than on cloudy days due to meteorological conditions. The results confirmed that limiting traffic emissions may increase O\textsubscript{3} concentrations in Guangzhou. Therefore, the focus should be on industrial, energy, and transportation emission mitigation and the influence of meteorological conditions to minimize O\textsubscript{3} 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\textsubscript{2.5}) has significantly decreased due to strict emission mitigation policies [2]. Ozone (O\textsubscript{3}) has become the most prevalent pollutant in China. The O\textsubscript{3} concentration has increased by 10.6% from 2015 to 2021 in 339 [3,4]. Excessive exposure to O\textsubscript{3} 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\textsubscript{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\textsubscript{3} pollution. The O\textsubscript{3} concentration has increased in the PRD since 2015 [20]. The O\textsubscript{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\textsubscript{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, and more O\textsubscript{3} is generated. Second, fewer aerosol particles are emitted...
during the weekend, resulting in less scattering and absorption of solar radiation. As a result, more O₃ 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, NOₓ 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)).

\[
O_2 + UV \rightarrow O + O \quad (1) \\
O + O_2 + M \rightarrow O_3 + M \quad (2) \\
NO_2 + hv \rightarrow NO + O \quad (3) \\
O_3 + NO \rightarrow NO_2 + O_2 \quad (4)
\]

In these processes, a dynamic equilibrium exists during the formation and consumption of O₃ by NOₓ. 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 NOₓ and O₃ and increasing the O₃ concentration.

\[
HO_2 + NO \rightarrow HO + NO_2 \quad (5) \\
RO_2 + NO \rightarrow RO + NO_2 \quad (6) \\
HO + RH + O_2 \rightarrow RO_2 + H_2O \quad (7) \\
RO + O_2 + hv \rightarrow HO_2 + RCHO \quad (8)
\]

If large amounts of NOₓ are emitted, HO and RO₂ react predominantly with NO₂ (Equations (9) and (10)); if small amounts of NOₓ 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 NOₓ 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.

\[
RO_2 + NO_2 \rightarrow RO_2NO_2 \quad (9) \\
HO + NO_2 \rightarrow HNO_3 \quad (10) \\
HO_2 + HO_2 \rightarrow H_2O_2 + O_2 \quad (11) \\
HO_2 + RO_2 \rightarrow RO_2H + O_2 \quad (12)
\]

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 NOₓ 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. NOₓ and VOC from traffic emissions are the main precursors of O₃. Therefore, it is necessary to investigate the relationship between traffic conditions and O₃ pollution. However, there are very few studies focusing on the influence of traffic situations on O₃. 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 factors are incorporated into the model one by one, and the statistical significance was evaluated. The insignificant factors were removed from the model.

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).
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.

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3. Results and Discussion

3.1. Temporal Variations of NO$_2$ and O$_3$

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 NO$_2$ differs from that of O$_3$. As shown in Figure 2d–f, the NO$_2$ 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 NO$_2$ concentration occurs at 20:00–22:00. The NO$_2$ 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. NO$_2$ reacts with VOCs to produce O$_3$, resulting in a decreasing trend at all three stations. The NO$_2$ concentration increases after 16:00 due to lower solar radiation and a decrease in the photochemical reaction [58–60]. During the night, the NO$_2$ 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/ m$^2$ in the cold season and 1806 kJ/ m$^2$ 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\textsubscript{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\textsubscript{2}, resulting in a higher NO\textsubscript{2} concentration [66]. However, the seasonal difference in the O\textsubscript{3} concentration is smaller than that of the NO\textsubscript{2} concentration. The reason is that O\textsubscript{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: O\textsubscript{3} concentrations at (a) HS station, (b) YJ station, and (c) LH station; NO\textsubscript{2} concentrations at (d) HS station, (e) YJ station, and (f) LH station.

3.1.2. Weekly Variations

The weekly variations in the O\textsubscript{3} and NO\textsubscript{2} concentrations at the three stations are illustrated in Figure 3. In general, the weekly trends of the O\textsubscript{3} and NO\textsubscript{2} concentrations are similar at three stations, but the average concentrations are different. As shown in Figure 3a, the O\textsubscript{3} concentration is significantly higher on weekends (Saturday and Sunday) than on weekdays (from Monday to Friday), indicating the weekend effect of O\textsubscript{3}. It is believed to be related to a change in the proportion of O\textsubscript{3} precursor emissions and other pollutant emissions from human activities [67]. Fewer human activities on weekends lead to lower PM\textsubscript{2.5} and a lower aerosol optical thickness and radiation extinction. Therefore, the O\textsubscript{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\textsubscript{3} formation on weekdays [70,71].

Differences in the O\textsubscript{3} concentration are observed at the three stations. The highest O\textsubscript{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\textsubscript{X} reducing the inhibition of NO on O\textsubscript{3} and leading to a higher O\textsubscript{3} concentration [72,73]. The YJ station is surrounded mostly by business and entertainment areas with frequent human activities. Large amounts of NO\textsubscript{X} are emitted from traffic inhibited O\textsubscript{3} formation. In addition, the titration effect of NO is stronger at the YJ station, leading to a slightly lower O\textsubscript{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 NO\textsubscript{2} concentration shows a significantly different pattern than that of the O\textsubscript{3} concentration. The NO\textsubscript{2} concentration is slightly higher on weekdays than on the weekend due to higher anthropogenic emissions, especially traffic emissions in urban areas [74–77]. The NO\textsubscript{2} 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.](image)

### 3.2. Influencing Factors

#### 3.2.1. Synergistic Variation of O3 and NO2

Figure 4 shows the scatterplots of the O3 and NO2 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 O3 concentration increases. However, differences are observed between daytime and nighttime. In the daytime, NO2 is consumed, and O3 is produced (Equations (2) and (3)). However, without a photochemical reaction during nighttime, O3 is converted to NO2 due to the titration effect (Equation (4)), leading to a lower O3 concentration. Due to the highly nonlinear and complex O3 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 O3 concentration at the roadside stations. Due to the absence of VOCs, a dynamic equilibrium exists between O3 and NOX in the atmosphere. Thus, O3 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 O3, resulting in high O3 pollution [82]. Controlling NOX emissions does not mitigate O3 pollution. Moreover, Guangzhou is in the VOC-limitation area [83,84]. Limiting vehicle emissions to reduce the NOX concentration may even increase the O3 concentration. Therefore, the focus should be on industrial, energy, and transportation emission mitigation and the influence of meteorological conditions to minimize O3 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\textsubscript{X} and VOC emissions are higher during frequent vehicle braking than during uniform driving. Thus, more O\textsubscript{3} precursors are emitted, leading to a significant positive correlation between O\textsubscript{3} concentration and travel-time ratio. The temperature is positively correlated with O\textsubscript{3} concentration as a result of O\textsubscript{3} formation. The negative correlation between the NO\textsubscript{2} and O\textsubscript{3} concentrations has already been discussed in Section 3.2.1. Moreover, a negative correlation is observed between vehicle speed and O\textsubscript{3} concentration. The fuel consumption is higher at higher speeds than at lower speeds, resulting in more precursor emissions and a higher O\textsubscript{3} concentration. Wind speed and O\textsubscript{3} concentration are negatively correlated because of the dilution effect. The O\textsubscript{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\textsubscript{3} generation.

Table 1. Pearson’s correlation coefficients between O\textsubscript{3} concentration and various factors.

| 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\textsubscript{2} (µg/m\textsuperscript{3}) | −0.220 *     | −0.153 **     |
| RH (%)                   | −0.495 **     | −0.226 **     |
| Solar radiation (J/m\textsuperscript{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 O\textsubscript{3} concentration and various factors.

| Model                      | Daytime Beta Value | p | Nighttime Beta Value | p |
|----------------------------|-------------------|---|-----------------------|---|
| 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\textsubscript{2} (µg/m\textsuperscript{3}) | −0.407         | 0.000       | −0.611                | 0.000       |
| RH (%)                     | −0.578            | 0.000       | −0.389                | 0.000       |
| Solar radiation (J/m\textsuperscript{2}) | -              | -           | 0.182                 | 0.000       |

The dependent variable: O\textsubscript{3} (µg/m\textsuperscript{3}).

The secondary pollutant O\textsubscript{3} is correlated with several factors. The vehicle speed and travel-time ratio are significantly correlated with the O\textsubscript{3} concentration, indicating the importance of traffic emissions on O\textsubscript{3} pollution in urban areas.

3.2.3. Case Study

As discussed in the previous section, traffic emissions affect the O\textsubscript{3} concentration but are not the dominant factor. Many studies demonstrated that solar radiation was a significant factor influencing O\textsubscript{3} formation. A case study was conducted to quantify the influence of solar radiation on O\textsubscript{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\textsubscript{3} concentration is substantially different on sunny and cloudy days at all three stations, indicating the predominant influence of solar radiation. The O\textsubscript{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 NO\textsubscript{2} concentration. In the daytime, there are no differences in the NO\textsubscript{2} concentration between sunny and cloudy days. However, the nighttime NO\textsubscript{2}
The pollutant concentrations and related parameters in the two periods.

| Period    | Station | O3 (µg/m³) | NO2 (µg/m³) | Travel-Time Ratio | Solar Radiation (KJ/m²) | RH (%) |
|-----------|---------|------------|-------------|-------------------|-------------------------|--------|
|           |         | Day Time   | Night Time  | Day Time          | Night Time              |        |
| Sunny days| HS      | 97.43      | 52.95       | 54.28             | 79.05                   | 1.14   | 1.03 |
|           | JY      | 94.70      | 63.45       | 48.80             | 63.66                   | 1.25   | 1.06 |
|           | LH      | 102.31     | 45.88       | 38.87             | 79.34                   | -      | -    |
| Cloudy days| HS | 37.30      | 21.15       | 52.34             | 53.10                   | 1.21   | 1.05 |
|           | JY      | 42.90      | 27.86       | 46.16             | 48.26                   | 1.29   | 1.08 |
|           | LH      | 41.70      | 25.75       | 36.99             | 41.59                   | -      | -    |

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.

4. Conclusions

This study evaluated the factors influencing the O3 concentration in traffic and urban background environments. The diurnal and weekly variation of the O3 and NO2 concentrations demonstrated a similar pattern at the three stations. These results were attributed to differences in the O3 generation mechanism, meteorological conditions, and emission sources. However, no significant differences in the O3 variation were observed between the three stations, implying that the O3 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 µg/m$^3$ 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$_x$ 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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