The current situation of surface layer ozone pollution in China's typical cities

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Abstract. Surface O\textsubscript{3} pollution mainly comes from the photochemical reaction, which is related to both meteorology and environment. Hence the formation and maintenance mechanisms of O\textsubscript{3} include both chemical and meteorological factors, resulting in a quite difficult forecast of surface O\textsubscript{3} pollution. In this study, the current situation of surface O\textsubscript{3} pollution in China's typical cities in 2014 is analyzed. The pollutants and meteorological factors before and after typical photochemical pollutions are statistically analyzed, in order to extract the forecast indicators of key parameters.

1. Introduction

Urban air pollutions usually present as coal smoke and photochemical smog. The former is caused by coal burning, with the main pollutants being particles and sulfur dioxide (SO\textsubscript{2}). And the latter is induced by the precursor pollutants such as nitrogen oxides (NO\textsubscript{x}), volatile organic compounds (VOCs) and so on, which are emitted from the automobile and petrochemical industry, with characteristic pollutants being strong oxidants, like O\textsubscript{3}\textsuperscript{1}.

In 1943, the first photochemical smog occurred in Los Angeles (the United States). After that, the smog episode happened in other regions such as North America, Japan, Australia and Europe. In China, photochemical pollutions came later than those in Europe and America, but with a much more complicated situation. At the end of 1970s, the photochemical smog was first detected in the Xigu petrochemical area in Lanzhou, and afterward comprehensive investigations of atmospheric physics and atmospheric chemistry on this phenomenon were carried out\textsuperscript{2,3}. The photochemical smog was found in Beijing in the summer of 1986 and the situation has become increasingly serious during the last 20 years \textsuperscript{4-6}.

According to the present studies, the main components of China's atmospheric complex pollutions are PM\textsubscript{2.5} and O\textsubscript{3}, namely haze and photochemical smog. O\textsubscript{3} can increase the atmospheric oxidability and can facilitate the oxidation of SO\textsubscript{2}, nitrogen dioxide (NO\textsubscript{2}) and VOCs in the atmosphere and the transformation from the gas-particles into particulates. As a result, it can increase the PM\textsubscript{2.5} concentration. Therefore, studying O\textsubscript{3} is of great significance for China's air pollution control.

Since 1940s, scholars from various countries have studied the formation mechanism of O\textsubscript{3}. The photochemical smog occurs in a very complex system with many variables, like the meteorological condition, the pollutants emission and the pollutants type, all of which affect the formation of O\textsubscript{3}. Therefore, researches were mainly carried out in smog chamber to exclude the influence of atmospheric conditions and various pollutants types. In addition, considerable progresses have been achieved in many fields, such as the variation law of the surface O\textsubscript{3} concentration\textsuperscript{6-13}, the relation between the vertical distribution of surface O\textsubscript{3} and the boundary layer structure\textsuperscript{8}, the correlation
between O$_3$ and meteorological conditions\cite{7,8,14,15}, the interaction of O$_3$ concentration and visibility (VIS)\cite{16,17}, the O$_3$ formation mechanism\cite{18} and the O$_3$ concentration forecasting model\cite{19}. For example, Zhu Bin\cite{20} found that winter and spring are the strongest periods for the stratosphere to transport to the troposphere, contributing the most to near-surface ozone, and from early summer to autumn, the stratosphere is weakly transported to the troposphere, contributing less to near-surface ozone. An Junlin's\cite{21,22} observational experiments show that the correlation coefficient between the ozone daily maximum concentration and the highest temperature on the ground, the maximum ultraviolet radiation on the ground, the average relative humidity during the day, and the average wind speed during the day are: 0.69, 0.46, 0.22, and 0.13, respectively, and when Beijing prevails southeast, southerly and westward, the O$_3$ concentration is higher. Ye Fang et al.\cite{22} found a significant monthly negative correlation between ozone and relative humidity, the annual correlation coefficient was -0.38, and ozone was significantly positively correlated with temperature, the annual correlation coefficient was 0.52. Wang Hong's\cite{23} research found that the average ozone concentration is higher than the annual average under the influence of six kinds of weather systems, such as the high pressure bottom, the high pressure back, and the ground back groove. And the average ozone concentration is lower than the annual average under the influence of four weather systems, such as the low vortex front, the subtropical high pressure edge, and the typhoon (tropical convergence zone). These indicate that the near-surface ozone concentration is affected by local meteorological elements, and it is prone to high ozone values under high temperature, high humidity and strong radiation conditions.

However, from the perspective of meteorological department, few domestic studies have focused on forecasting the O$_3$ concentration variation, by using the meteorological factors. Moreover, in the national level environmental weather forecast service, both the source characteristics of precursor pollutants and the meteorological conditions of photochemical pollution vary dramatically from place to place. Therefore, it is necessary to investigate the current situation of O$_3$ pollution and its correlation with precursors, aerosols and meteorological conditions in typical regions and cities in China.

In this paper, the spatio-temporal characteristics of the O$_3$ concentration distribution in 2014 are analyzed. Taking Beijing, Shanghai, Guangzhou and Chengdu as the typical cities of Beijing-Tianjin-Hebei region, the Yangtze River Delta, the Pearl River Delta and Sichuan-Chongqing region respectively, the number of days with overproof ozone in different months and the monthly mean O$_3$ concentrations are discussed. Besides, the interactions between O$_3$ and PM$_{2.5}$ are explored, and the linear relationships among temperature (Temp), total cloud cover (TCC), relative humidity (RH), wind speed (WS) and O$_3$ concentration are analyzed, which can provide certain technical supports for the monitoring and forecast of photochemical smog and can offer a scientific basis for the urban air pollution prevention and control.

2. Data and method

2.1. Data

The environmental monitoring data are obtained from the hourly environmental observation data at the state controlling air sampling sites of China national environmental monitoring center (http://106.37.208.233:20035/), including PM$_{2.5}$, PM$_{10}$, SO$_2$, NO$_2$, carbon monoxide (CO), O$_3$ and hourly air quality index (AQI) concentration. The specific sites are the 12 monitoring stations in Beijing (from the north to the south), 10 monitoring stations in Shanghai (from the west to the east) and 11 monitoring stations in Guangzhou (from the south to the north).

The meteorological data are derived from the conventional surface observation data in Beijing Station (No. 54511), Shanghai Station (No. 58362), Guangzhou Station (No. 59287), and Chengdu Station (No. 56187), including VIS, temperature, atmospheric pressure (Pascal, Pa), RH, weather, TCC, wind direction (WD) and hourly mean WS.
2.2. Data processing
To understand the situation of photochemical pollutions in the four super cities, the seasonal and inter-annual variations of O$_3$ concentration should be first identified. In this paper, the spring is defined as March to May, the summer as June to August, the autumn as September to November and the winter as December to the next February. Firstly, the weather data of rainfall and sand dust is screened and excluded accordingly. Secondly, the weather types are mainly classified as sunny day, cloudy day, haze, and light fog. In this paper the, O$_3$ evaluation indices refer to the Ambient Air Quality Standard (GB 3095 - 2012) and Technical Regulation on Ambient Air Quality Index (HJ633-2012), so as to correctly analyze the characteristics of the number of days with overproof ozone and O$_3$ concentration variations.
3. Results

3.1. The spatio-temporal distribution of O$_3$ concentration and the number of days with overproof ozone

3.1.1. The monthly numbers of days with overproof ozone

Figure 1 presents the monthly number of days with overproof ozone in 2014. From April, the number of days with overproof ozone begins to increase in southern North China, Huanghuai (The Huanghuai area generally refers to the lower reaches of the Yellow River and the northern part of the Huaihe River Basin. The main scope is in the central part of Henan Province, the north-central part of Anhui
Province, the south of the Yellow River in Shandong Province and the north of the Huaihe River in Jiangsu Province.), Jianghuai (The Jianghuai area mainly refers to the area south of the Huaihe River and the north of the lower reaches of the Yangtze River in Jiangsu Province and Anhui Province) and other regions (Figure 1). Following the South China rainy season in May, the solar radiation weakens, and days with overproof ozone decrease in the Pearl River Delta but increase in southern North China, Huanghuai, Jianghuai and other regions. During the plum rain season in June and July, the radiation weakens and the days with overproof ozone lessen in Jianghuai and Jiangnan regions, while the overproof days show an increasing trend in North China. At the end of the flood season in September and October, with the radiation in Jiangnan and South China increasing, the overproof days exhibit an enhancement in Jiangnan and South China but a decline in North China.

In 2014, the annual mean O₃ concentration is 55.8 μg/m³ in Beijing, with a minimum daily mean value 2 μg/m³ and a maximum one 188 μg/m³. The annual mean O₃ concentration is 66.9 μg/m³ in Shanghai, with a minimum daily mean value 10 μg/m³ and a maximum one 148 μg/m³. The annual mean O₃ concentration in Guangzhou is 48.6μg/m³, with a minimum mean daily value 8 μg/m³ and a maximum one 132 μg/m³. The annual mean O₃ concentration is 49.5 μg/m³ in Chengdu, with a minimum daily mean value 10 μg/m³ and a maximum one 184 μg/m³.

3.1.2. The monthly O₃ concentrations in the typical cities
The monthly O₃ concentrations of the four typical cities are analyzed. The O₃ concentration from May to August is higher in Beijing, which is related to its high air temperature and strong solar radiation in summer. The O₃ concentration from June to August is relatively lower in Shanghai due to the radiation decrease during the plum rain season in Jianghuai and Jiangnan regions. The O₃ concentration is lower in Guangzhou from March to May, which may be related to the South China flood season. The temperature there is still high at the end of flood season in October, when the O₃ concentration reaches the peak of the year. The trend in Chengdu is similar to that in Beijing with highest O₃ concentration from May to August, but its amplitude is lower than that of Beijing, which may be caused by the abundant water vapor, cloud, fog and less radiation in the Sichuan Basin.

3.1.3. The daily variations of O₃ concentration in typical cities
The daily variations of O₃-1h concentration in four cities were also analyzed. According to the annual mean value, the peak values of O₃-1h concentrations in Beijing and Chengdu appear at 16:00, but they appeared at 17:00 in these two cities according to the summer mean value. Besides, for either annual mean or summer mean, the peak value appears at 16:00 in Shanghai and at 17:00 in Guangzhou. The summer mean hourly O₃ concentrations in four cities are higher than corresponding annual mean values due to the higher temperature and stronger radiation in summer. But in Beijing and Chengdu, compared with Shanghai and Guangzhou, the O₃ concentrations at every hour in summer are significantly higher than those of the annual mean, and the difference is obvious in the morning and night. The peak value of the annual mean diurnal variation in Beijing is similar to those in Shanghai, Guangzhou and Chengdu, but the peak value of the summer mean diurnal variation in Beijing is significantly higher than that in the other three cities, which may be related to the strong summer radiation and scarce precipitation in Beijing in summer.

3.2. Correlations between O₃ concentration and relative humidity, total cloud cover (radiation), 2-m temperature and wind speed in the typical cities
In this paper, based on the statistical analyses of many pollution processes and taking Chengdu as an example, the correlations between O₃ and RH (relative humidity), TCC (total cloud cover, represent the radiation), 2-m temperature and WS (wind speed) are analyzed. The data in the whole year is used and the influence of precipitation is excluded.

As shown in Figure 2, the O₃ concentration shows an obvious inverse correlation with RH, and a consistent positive correlation with 2-m temperature. There is no obvious linear relationship between the O₃ concentration and the TCC, indicating that the TCC cannot properly represent the radiation
quantity. And then it can be further studied according to different cloud types. The relationship with WS can be investigated in different ranges. In the small wind range (≤ 2 m/s), the O$_3$ concentration varies little with the WS, ranging from 0～300 μg/m$^3$. But when the WS exceeds 2 m/s, the O$_3$ concentration obviously decreases as the WS increases. Therefore, it indicates that WS can indicate the horizontal diffusion capacity, and its inverse correlation with O$_3$ concentration is reasonable, but there is little correlation between them in a small WS range.

![Figure 2](image.png)

**Figure 2.** Correlations between O$_3$ concentration and RH(a), TCC(b), 2m Temp(c) and wind speed(d).

### 3.3. A typical case in Beijing

A photochemical smog process in Beijing from May 30 to June 2, 2014 is analyzed, so as to better understand the formation and development mechanisms of photochemical smog.

From the average circulation situation on 500hPa as shown in Figure 3(b), Beijing is controlled by the southerly flow on the backside of the high ridge on May 30 and May 31, which is conducive to the temperature increase. On the sea level pressure field as shown in Figure 3(a), the isobars in the North China Plain are sparse without any obvious weather system passing over it. According to the mean temperature field on 850hPa as shown in Figure 3(c), North China is controlled by the warm tongue with a higher temperature than before. According to the average specific humidity field on 850hPa as shown in Figure 3(d), the specific humidity of Beijing is only 4 g/kg, relatively poor.

From the correlations between O$_3$ concentration and the meteorological elements in Figure 4, it is suggested that O$_3$ concentration and 2-m temperature have a relatively similar variation in the whole process, while O$_3$ concentration have an inverse correlation with VIS and RH. From May 30 to May 31, the O$_3$ concentration is high and over 250 μg/m$^3$ during some periods, and VIS and RH are relatively low. But in the evening of June 1, with the arrival of weak precipitation, the RH increases and the O$_3$ concentration decreases rapidly. During the whole process, no obvious relation exists between O$_3$ concentration and WS.
Figure 3. Analysis of the atmospheric circulation situation from May 20 to May 31, 2014 (a. sea level pressure; b. Potential height at 500hPa; c. Temperature at 850hPa; d. Specific humidity at 850hPa).

Figure 4. The correlations between O$_3$ concentration and typical meteorological elements (VIS, 2-m Temp, WS, RH) from May 20 to June 2, 2014.

Figure 5 presents mixing layer height variations under different weather conditions. On May 30, Beijing is dominated by clear or cloudy days. The mixing layer height increases rapidly after sunrise, surpasses 1600 m occasionally in the afternoon. At the same time, the O$_3$ concentration also increases.
rapidly, reaching over 250 μg/m³. On May 31, haze dominates Beijing, which is probably caused by the increase of O₃ concentration on the previous day, promoting the photochemical reaction and the generation of a large number of secondary pollutants and resulting in the PM₂.₅ concentration increase. Compared with that in May 30, RH on May 31 slightly increases, so the VIS decreases correspondingly. It is notable that when the haze occurs, the mixing layer height is lower than that on the cloudy day, but the O₃ concentration continues to increase under high temperature. After May 31 midnight, a small shower occurs in Beijing, clearing the haze and decreasing O₃ concentration. Although the diurnal variation in temperature in the daytime of June 1 leads to the increase in O₃ concentration, it is significantly lower compared with those in the last two days. The second shower before the midnight of June 1 results in a continuous decrease in O₃ concentration.

Figure 5. The correlation between O₃ concentration and mixing layer heights under different weather conditions from May 20 to June 2, 2014.

4. Conclusions and discussions
In this paper, the current situation of photochemical smog pollution in typical cities of China is analyzed, and the formation and maintenance mechanisms of the photochemical smog, including chemical and meteorological factors, are discussed. Moreover, the pollutant elements and meteorological factors before and after several typical photochemical pollution processes are statistically studied, and the forecast indicators of key parameters are extracted. The correlations between O₃ concentration and several typical meteorological factors are analyzed by statistical methods. The conclusions are as follows:

(1) The previous studies of air pollution mainly focused on the air pollutants and particulates in China. O₃ will exert more influence on the air quality than PM₂.₅ under the specific conditions, as PM₂.₅ and O₃ evaluation indices are added in Ambient Air Quality Standard. The study and control of O₃ will also attract more and more attentions.

(2) The diurnal variation trend of hourly O₃ concentration is obvious, which is positively related to the solar radiation intensity. The O₃ concentration is high in the daytime and low in the nighttime, with the peaks mainly existing during 14:00-16:00 and the low values mainly appearing during 4:00-6:00.

(3) The seasonal variation trend of O₃ concentration is obvious. Without the influence of precipitation, the peaks mainly happen in May to October, and the low values mainly appear in November to the next April, with slight differences in different regions.

(4) Attention should be paid to the fact that the O₃ pollution in Beijing is heavier than in southern cities like Shanghai and Guangzhou, which is mainly due to the poor water and vapor conditions in the middle and low levels, the thin cloud layer and the strong radiation in Beijing.

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