Variation Characteristics Mathematical Calculation of O3 and Its Relationship with Meteorological Factors by Big Data Technology

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Abstract. Based on the data of environmental monitoring stations and meteorological stations in Qinhuangdao from May 2017 to May 2020, the variation characteristics of O3 and precursors (NO2 and CO) as well as their relationship with meteorological elements were analyzed. The results showed that the daily average concentration of O3-8 h in Qinhuangdao increased year by year. The monthly average concentration of O3-8 h was high in summer and low in winter, and the peak appeared in June. The diurnal variation of O3 concentration was unimodal structure, and the concentration increased in the afternoon, but it decreased at night. The concentration of NO2 and CO was inversely correlated with O3, and the peak value of NO2 in March could be related to frequent cold air activity and increased burning of loose coal. The meteorological elements favorable for the occurrence of ozone pollution weather in Chengde were total solar radiation irradiance greater than 1000W/m², the daily maximum temperature greater than 33°C, and the daily minimum relative humidity less than 40% and 65%~80%, southerly wind or southwest wind.

Keywords: Ozone concentration, Variation characteristics, Meteorological Factor, Qin Huang-dao City.

1. Introduction
Ozone (O3) 90% was mainly distributed in the stratospheric atmosphere. The content of O3 in the troposphere was very low, accounting for only 10% of the total atmospheric O3 [1]. O3 was mainly composed of nitrogen oxides (NOx), carbon monoxide (CO) and volatilization. (VOCs), etc. were generated by photochemical reactions in the sun [2]. O3 could stimulate the human respiratory system, and it could destroy the immune system, which caused inflammation and respiratory diseases, etc., and seriously endangered human health [3-4]. In addition, O3 pollution could also cause crop yield reduction [5], increase the greenhouse effect [6], and even affect climate change [7].
For many years, the research and prevention and control of air pollution in my country had mainly focused on particulate pollution. However, with the increase of O₃ concentration near the ground, the temporal and spatial distribution characteristics, influencing factors and mechanism of O₃ pollution had attracted the attention of experts and scholars. Many scholars had shown that the changing law of O₃, in recent years, the concentration of O₃ near the ground in my country had been on the rise. The 90th percentile average of the largest O₃-8h average mass concentration in major cities across the country increased from 139 μg/m³ in 2013 to 167 μg/m³ in 2017 [8]. From the perspective of seasonal changes, O₃ pollution was more serious in summer in major cities, followed by spring and autumn, and the lightest pollution in winter from 2014 to 2017 [9]. From the perspective of monthly changes, O₃ pollution in Beijing-Tianjin-Hebei was mostly "single-peak", with peaks concentrated in May-July [10]. From the perspective of diurnal changes: the diurnal change of O₃ was a single-peak distribution, and the concentration was higher in the afternoon, and the photochemical reaction was enhanced, resulting in a gradual increased in the O₃ concentration, while O₃ was consumed under the titration effect [11] from afternoon to night, and the O₃ concentration gradually reduced.

Meteorological elements were also important factors that affected the characteristics of O₃ pollution. Meteorological elements such as temperature, humidity, wind direction and wind speed, and weather systems of different scales had certain effects on the generation and transmission of O₃ precursors. The O₃ concentration in Beijing area was inversely proportional to air pressure, humidity and visibility, and directly proportional to wind speed and temperature [12]. Qinhuangdao was a national tourist city and an ecologically civilized city. In recent years, the peak ozone concentration has increased year by year, heavy pollution had emerged from scratch, and the overall trend was on the rise. From 2017 to 2020, there were 7 cases of ozone pollution in Qinhuangdao City. Therefore, in response to the increasing ozone pollution in Qinhuangdao City, Hebei Province, this article will analyze in detail the characteristics of the change of ozone concentration in Qinhuangdao City and the relationship with meteorological elements, and provide certain technical support for the forecast and early warning of ozone pollution in Qinhuangdao City.

2. Data sources and methods

Using the concentration monitoring data of ozone and precursors (NO₂, CO) from May 2017 to May 2020 at Qinhuangdao Environmental Monitoring Center, the five monitoring points were the Municipal Monitoring Station, Beidaihe Environmental Protection Bureau, The first pass, the construction building, and the civilization were located in the northeast, northwest, southeast and southwest of the urban area in turn, which could characterize the changes in urban pollutant concentration. Meteorological data were the hourly surface temperature, relative humidity, wind direction and wind speed, sea level pressure and sunshine hours at the Qinhuangdao Weather Station from May 2017 to May 2020. The division of seasons in the article: Spring is from March to May, summer is from June to August, autumn is from September to November, and winter is from December to February of the following year. The daily maximum 8 h ozone sliding average represents the daily ozone mass concentration, and the city-wide average refers to the average of five environmental monitoring points.

3. Results and discussion

3.1. Overview of O₃, NO₂, and CO pollution

The Variation characteristics in the annual daily average concentration of O₃, NO₂ and CO in Qinhuangdao City from May 2017 to May 2020, it could be seen from Figure 1 that the concentrations of the three pollutants all change periodically, the concentration of O₃ tended to increase, while the concentration of NO₂ and CO decreased year by year. This was mainly because the number of motor vehicles in Qinhuangdao City had increased year by year. As of 2020, the number of vehicles in our city (850,000) and the number of new motor vehicles were increasing every day, which led to increased vehicle exhaust emissions and causes secondary pollutant concentrations increase. The annual change trend of O₃ was relatively obvious, increasing in spring, reaching the highest in summer, gradually
decreasing in autumn, and decreasing to the lowest in winter. The changes of NO2 and CO were similar, with higher concentrations in winter and spring, and lower concentrations in summer and autumn.

![Graph showing annual variation of daily mean concentrations of O3, NO2 and CO from May 2017 to May 2020 in Qinhuangdao](image)

**Figure 1.** Annual variation of daily mean concentrations of O3, NO2 and CO from May 2017 to May 2020 in Qinhuangdao

### 3.2. Seasonal changes of O3, NO2 and CO

The seasonal variation curve of O3, NO2 and CO and concentration in Qinhuangdao from May 2017 to May 2020, It could be seen from Figure 2 that the seasonal variation of O3 presents an "inverted U" pattern, with the overall concentration being high in spring and summer, and low in autumn and winter. The concentration from April to September was relatively high, all higher than 100μg/m³. The concentration in June was the highest at 157.9μg/m³, while the concentration of O3 from January to March and October to December was relatively low. The lowest concentration appeared at 12. Month, it was 40.2μg/m³. In addition, the O3 concentration from July to August was lower than June. Because the heavy rains in our city were mainly concentrated in July and August. Although the strong solar radiation and high temperature in summer were conducive to the conversion of ozone, the precipitation process caused the photochemical reaction rate to decrease. Made its average concentration value lower than the concentration value in June.

The annual changes of NO2 and CO both showed obvious U-shaped characteristics. The concentration of NO2 was low from April to October, and the minimum was 30.1μg/m³ in July; the concentration was relatively high from November to January, and the maximum was 57.5μg/m³ in December; however, March was relatively large, and the extreme value of 62.7μg/m³ appeared in March 2016. The main reason was that at the end of the heating period in March, the weather was unstable and affected by cold air, and the amount of coal burned in rural areas increased. For CO, the concentration from April to October was relatively low and had not change much. The maximum occurs in January, which was 1.88μg/m³. For the high concentration of CO and NO2 in winter, the main reason was that the winter is a heating period. Because of the influence of coal burning, CO and NO2 emissions are higher than other seasons, and the conversion efficiency of CO and NO2 in winter was low, which increased the concentration of CO and NO2.
3.3. Daily changes of \(O_3\), \(NO_2\) and \(CO\)

The daily variation curve of the average concentration of \(O_3\), \(NO_2\) and \(CO\) in different seasons in Qinhuangdao City. The concentration value at each moment was the average concentration of all the moments in this season. Seasonal division: spring is from March to May, and summer is from June to August, autumn is from September to November, and winter is from December to February of the following year, as shown in Figure 3.

**Figure 2.** Monthly changes of \(O_3\), \(NO_2\) and \(CO\) concentrations from May 2017 to May 2020 in Qinhuangdao

**Figure 3.** Diurnal variation of \(O_3\), \(NO_2\) and \(CO\) in different seasons from May 2017 to May 2020 in Qinhuangdao
It could be seen from Figure 3 that the daily change value of $O_3$ concentration in summer was the largest, the daily change value in spring was second only to summer, the daily change value in autumn was smaller, and the daily change value in winter was the smallest. As a result of solar radiation and temperature which were the key meteorological factors that caused daily changed in $O_3$ concentration. The possible reason that spring was higher than autumn was that the rainy weather process in autumn was more than that in spring, and the temperature dropped faster in autumn, which caused its photochemical reaction to be weaker than that in spring. The diurnal variation curve of $O_3$ presents an obvious single-peak structure, and the concentration during the day was significantly higher than that at night. The peak appeared at 16 o'clock, which was 128.8μg/m$^3$; the lowest concentration at 6 o'clock was 43.3μg/m$^3$. The diurnal changes of NO$_2$ and CO concentration were higher in autumn and winter, and lower in spring and summer. The diurnal variation curve of NO$_2$ presented a double-peak structure. The peak period was from 06 to 08 and from 21 to 23. The highest concentration was 43.3μg/m$^3$ at 08, and the lowest concentration was 17.5μg/m$^3$ at 14 o'clock. Similar to the change of NO$_2$, the maximum CO concentration was 878.2μg/m$^3$ at 08 o'clock, and its lowest concentration was 513μg/m$^3$ at 17. The bimodal changed in the concentration of CO and NO$_2$ were mainly due to the emission of motor vehicle exhaust. The appearance of the two peak periods was closely related to the morning and evening peaks.

3.4. The influence of meteorological conditions on $O_3$ concentration

The contribution of precursor pollution sources and solar radiation had an important influence on the changes of $O_3$ concentration. At the same time, atmospheric circulation and meteorological elements played an important role in the formation, precipitation, transmission and dilution of $O_3$. Solar radiation was a key factor in determining the production of $O_3$, and the concentration of $O_3$ lagged behind changes in solar radiation intensity. As an important indicator of solar radiation intensity, temperature had significant seasonal differences, the highest in summer and the lowest in winter, which was similar to the seasonal variation of $O_3$ concentration. Relative humidity was the relative water content in the atmosphere, reflecting the degree of water vapor saturation. It was mainly affected by water vapor and temperature. It was higher at night and had a minimum value in the afternoon. Relative humidity had an important impact on the formation and deposition of $O_3$ pollutants. Wind direction could reflect the direction of pollutants transmission, wind speed could reflect the strength of atmospheric boundary layer turbulence, increasing wind speed was conducive to the diffusion of pollutants, while the height of the boundary layer rised, which was conducive to the downward transmission of $O_3$ pollutants in the upper layer. Meteorological factors affected the occurrence of photochemical reactions and the transmission of pollutants, thereby causing changes in $O_3$ concentration in the near-surface layer. $O_3$ was generated from primary pollutants through a photochemical reaction under solar radiation conditions. With the increase of solar radiation, the temperature gradually rised, and at the same time increases the rate of atmospheric photochemical reactions, resulting in an increase in ozone concentration.

3.4.1. Solar radiation and $O_3$ concentration. According to statistics, the daily $O_3$-8h concentration from May 2017 to May 2020 corresponded to the maximum daily total radiation irradiance in Qinhuangdao. It could be found that the higher $O_3$ concentration was mainly concentrated in the case of strong total solar radiation irradiance. The correlation coefficient $r=0.49$, showing a significant positive correlation. When the total radiation irradiance is less than or equal to 750 W/m$^2$, the average concentration of $O_3$-8h was the lowest, only during 92-102μg/m$^3$. The total radiation irradiance increased by 50 W/m$^2$, the average concentration of $O_3$-8h increased by 10-20μg/m$^3$. When the total radiation irradiance was greater than 1000 W/m$^2$, the average concentration of $O_3$-8h exceeded 160μg/m$^3$. Therefore, the total radiation irradiance was greater than 1000 W/m$^2$, which mostly occurred in the spring and summer, and it happened to be the most serious time when $O_3$ exceeded the standard in Qinhuangdao City.

3.4.2. Maximum temperature and $O_3$ concentration. As the daily maximum temperature increased, the $O_3$-8h concentration gradually increased. When the daily maximum temperature was greater than 20℃, the $O_3$-8h concentration increased gradually with the increased in temperature. The correlation
coefficient between daily maximum temperature and O₃-8h concentration was r=0.69, and there was a significant positive correlation. When the highest temperature of the day was less than 15°C, the average concentration of O₃-8h was less than 83μg/m³. When the daily maximum temperature was from 15°C to 25°C, and the daily maximum temperature rose by 5°C, the average concentration of O₃-8h would increase by 30μg/m³. When the highest temperature of the day was more than 30°C, the average O₃-8h concentration was more than 188μg/m³. The higher the temperature, the stronger the solar radiation, the stronger intensity of the photochemical reaction, produced the higher the O₃ concentration. The seasons of the highest temperature was more than 30°C which mostly occured from May to August, and it coincided with the highest O₃ concentration in Qinhuangdao City.

![Figure 4. Fitting relationship of O₃ concentration between daily maximum temperature and relative humidity from May 2017 to May 2020 in Qinhuangdao](image)

3.4.3. Relative humidity and O₃ concentration. The daily minimum relative humidity had a negative correlation with the O₃-8h concentration, the correlation coefficient was r=-0.18, the average O₃-8h concentration had two peaks with the change of relative humidity, when the relative humidity was less than 40%, the average O₃-8h concentration was during 137-142μg/m³, when the relative humidity was 65% ~ 80%, the average concentration of O₃-8h was 127μg/m³. When the relative humidity was greater than 80%, the average concentration of O₃-8h was less than 86μg/m³, indicating that higher relative humidity was not conducive to the generation of O₃. This was mainly because under the action of water vapor, the solar radiation reaching the near-surface layer would be attenuated due to the extinction mechanism; high humidity was conducive to the dry deposition of O₃, thereby achieving the effect of eliminating O₃; at the same time, the OH contained in water vapor in the air under high relative humidity Free radicals such as, HO₂ could quickly decompose O₃ into O₂, thereby reducing the concentration of O₃ in the near-surface atmosphere.

3.4.4. Wind direction and speed and O₃ concentration. The O₃ concentration was affected by the wind direction and speed. Under the control of the southerly airflow, O₃ pollution was the most serious (Fig.5). The average concentration of O₃-8h was 185μg/m³. At the same time, the wind speed of the southerly wind was also strong; The average concentration of O₃-8h was 179μg/m³. The average O₃-8h concentration corresponding to other wind directions were relatively low. Because the southwest of Qinhuangdao City was Tangshan and the south-central part of Hebei Province. They had relatively serious pollution, which was conducive to the transportation of pollutants such as O₃ and its precursors to the Qinhuangdao area; the northwest and northerly air currents carried Mongolia’s cold, the southward movement of the air WAs conducive to the dilution and diffusion of pollutants; the easterly airflow comes from the Bohai Bay, with abundant water vapor and relatively clean, and it was also not conducive to the generation and accumulation of O₃ pollutants.
4. Conclusion

1. The daily average concentration of O₃-8h in Qinhuangdao City showed a trend of increasing year by year; the monthly average O₃-8h concentration presented seasonal variation characteristics of high in summer and low in winter, and the peak occurs in June; the daily variation was a single peak structure, and the concentration in the afternoon rised and it fell at night. NO₂ presented the opposite trend, with a peak in March, frequent removal of cold air, and increased burning of loose coal. CO presented a "U"-shaped structure, which had an inverse correlation with O₃.

2. Meteorological elements played an important role in the formation, precipitation, transmission and dilution of O₃. The meteorological elements that were conducive to the occurrence of O₃ polluted weather in Qinhuangdao City were total solar radiation irradiance more than 1000 W/m², daily maximum temperature greater than 33℃, no precipitation occurs, and the minimum daily relative humidity was less than 40% and 65% to 80%, affected by southerly or southwesterly winds.

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