Characteristics of PM$_{2.5}$ Pollution with Comparative Analysis of O$_3$ in Autumn–Winter Seasons of Xingtai, China

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Abstract: Pollutants emission, meteorological conditions, secondary formation, and pollutants transport are the main reasons for air pollution. A comprehensive air pollution analysis was conducted from the above four aspects in the autumn–winter seasons of 2017–2018 and 2018–2019 at Xingtai, China. In addition, the relationship between PM$_{2.5}$ and O$_3$ was also studied from the aspects of secondary formation and meteorological conditions to find the rules of cooperative management of PM$_{2.5}$ and O$_3$ combined pollution. Taking measures of concentrated and clean heating and controlling biomass burning could make the concentrations of EC, K$^+$ and SO$_4^{2−}$ decrease. The variation trends of PM$_{2.5}$ and O$_3$ concentration in the autumn–winter season of Xingtai were different, and with the increase in secondary formation effects, the concentration of O$_3$ decreased. Furthermore, the key meteorological conditions that affected O$_3$ and PM$_{2.5}$ formation were temperature and relative humidity, respectively. The relationships of NOR (nitrate oxidation rate) and SOR (sulfate oxidation rate) against temperature presented a “U” shape, suggesting that gas-phase oxidation and gas–solid-phase oxidation were all suppressed at a temperature of around 4 °C. The cities located in the east had more pollutant transporting effects during the pollution processes of Xingtai, and the main transport routes of O$_3$ and PM$_{2.5}$ were not all the same.

Keywords: PM$_{2.5}$; O$_3$; heavy metal; secondary formation; meteorological condition

1. Introduction

The accelerated urbanization, booming economy, increased vehicles, and developing industry has brought urgent environmental problems worldwide [1–3]. Air pollutants released from human production and life not only induce severe health problems, from respiratory illnesses to cardiovascular diseases but also have adverse impacts on ecosystems and transportation [4,5]. In the past several years, as one of the fastest developing countries in the world, China has also suffered a series of air pollution issues, such as acid rain, sandstorm, fine particulate matter (PM$_{2.5}$), and ozone (O$_3$) [6–9]. The first two issues have been controlled through the unremitting efforts of the government and the people of China. However, the air pollution issues of PM$_{2.5}$ and O$_3$ are still to be settled.

China has issued a series of control measures to mitigate PM$_{2.5}$ pollution, such as the Air Pollution Prevention and Control Action Plan (APPCAP) and emergency measures in autumn and winter acts. Moreover, a large amount of human and financial resources has been put into mitigating PM$_{2.5}$ pollution. The project for finding out the cause and control methods of heavy air pollution was supported by the prime minister’s fund and was conducted from 2017–2019. Moreover, twenty-eight science teams were stationed at Beijing–Tianjin–Hebei and its surrounding areas to carry on the on-site work and help the local government to improve air quality. However, with the sharp decrease in PM$_{2.5}$ levels, O$_3$ concentration had an upward trend. Thus, it is of great importance to analyze
the pollution characteristics of PM$_{2.5}$ and the interactive relationship between PM$_{2.5}$ and O$_3$ to offer references for scientific research and introducing policy for coordinated control of PM$_{2.5}$ and O$_3$ in the future.

Local emissions, unfavorable climate conditions, secondary formation, and regional transport are four main reasons for the formation of both PM$_{2.5}$ and O$_3$ pollution. According to the study of main sources of PM$_{2.5}$ from 2005 to 2014, emission from anthropogenic factors, thermal power, biomass burning, and industrial production constituted the largest proportion of PM$_{2.5}$ emission [10]. In China, emission reductions in 2014 and 2015 effectively reduced PM$_{2.5}$ concentrations by 23.9 and 43.5 µg/m$^3$, respectively, but those were partially counteracted by unfavorable meteorology. However, emission changes led to 13.4 and 16.5 ppb increase of 8h-O$_3$ in 2014 and 2015 [11]. Strong sensitivities of PM$_{2.5}$ and O$_3$ to meteorology can be learned through changes in physical and chemical processes [12]. The decreased planetary boundary layer height (PBLH) may restrain vertical mixing and lead to the accumulation of particles [13,14]. Moreover, it also decreases the environmental capacity of PM$_{2.5}$. Wind, temperature, and precipitation all have obvious effects on air pollution. A decreasing trend in wind is unfavorable for air pollution dispersion [15,16]; an increase in temperature or solar radiation can enhance chemical reaction rates of O$_3$ [17,18]; less precipitation means fewer wet removal processes, which can also increase air pollutant concentrations [19,20]. Usually, a severe pollution episode is affected by high concentrations of primary source emissions and secondary pollutants together, which further supply a large number of precursors for heterogeneous reactions [21]. Furthermore, these reactions can change the atmospheric oxidation and have obvious impacts on the components of PM$_{2.5}$. The high concentrations of NO$_x$ during the haze episodes play an important role in the secondary transformation of SO$_2$ into sulfate aerosols [22]. On the other side, the increasing trend for O$_3$ is hard to control regardless of the reduction in precursors because O$_3$ pollution is mainly formed by secondary formation [23]. Regional transportation is also an important factor affecting local air quality [24]. A pollution conveyor belt was found across the Beijing–Tianjin–Hebei region to the northeast China region. By calculation, the contribution of the Beijing–Tianjin–Hebei region to PM$_{2.5}$ in Shenyang could reach about 30–60% [25].

Xingtai is an industrial city of the Hebei province located in the south of the Beijing–Tianjin–Hebei region and the east side of the Taihang mountain chain, which is a natural parclose for pollutants diffusion of Xingtai. Thus, Xingtai is a typical sample city for the research of air pollution. Equipment manufacturing, building materials, coal, and salt chemical industries are the pillar industries of Xingtai. There are many large iron and steel, cooking and chemical, and glass industries around the main urban areas, which have obvious disadvantageous effects on air quality. The Xingtai government has made great efforts in industrial restructuring, energy structure optimization, improvement in the structure of transport, surface source pollution control, and response to heavy pollution weather to improve the air quality in recent years. Through a series of air pollution control action plans, the air quality of Xingtai has gradually improved. In the year 2019, the concentration of PM$_{2.5}$ was 65 µg/m$^3$, which had a 50% decrease compared to that in the year 2014. The heavy pollution days for Xingtai also decreased year by year, and in the year 2019, the serious, heavy, medium, and slight pollution days had decreased 31, 44, 9, and 107 days compared to the year 2014.

Although the air quality has obviously improved, the annual PM$_{2.5}$ concentration is still 1.85 times the air quality secondary standard of China in 2019. Air pollutant excessive emissions, unfavorable terrain, high secondary formation rate, and meteorology conditions together lead to frequent and severe air pollution in Xingtai. Thus, it is meaningful to make a comprehensive analysis of air pollution to make clear the air pollution characteristics of heavy industry cities, such as Xingtai. The chemical components of PM$_{2.5}$ in the autumn–winter seasons of 2017–2018 and 2018–2019 were analyzed. In order to illustrate the effects of meteorological conditions and secondary conversion on PM$_{2.5}$ pollution, Kendall’s tau coefficient was used to present the coefficient relationships between factors. In addition,
the variation trends of the concentration of PM$_{2.5}$ and O$_3$ and the coefficient relationships of meteorological conditions with O$_3$ were also illustrated. The cluster of backward flow trajectories and air pollution of O$_3$ and PM$_{2.5}$ were used to describe the main transmission routes of the pollutants of the pollution processes in the autumn–winter seasons.

2. Materials and Methods

2.1. Sampling of PM$_{2.5}$

2.1.1. Sampling Position, Period, and Samples Collection

Xingtai is a typical industrial city, which has lots of glass, cement, and coking industries. Xingtai is also a northern city dominated by a north wind. Thus, many industrial plants are located in the south county of Shahe. In order to study the effects of transfer, emission, and weather conditions, three sampling sites were located in the main city (Yizhong Station, YZ) and the upwind (Neiqiu Station, NQ) and downwind Shahe Station, SH) direction of the main city during the autumn–winter season (See Figure 1). Sampling points all lay within 1.5–15 m from the ground in strict accordance with the provisions of the National Technical Specification for Layout of Ambient Air Quality Monitoring Points HJ 664-2013.

![Sampling sites’ locations.](image)

The sampling periods were two autumn–winter seasons which were from 15 October 2017 to 30 January 2018 and 15 October 2018 to 30 January 2019. Daily PM$_{2.5}$ samples were collected continuously from 09:00 to 08:30 of the next day, and the sampling time was 23.5 h. Six hundred forty-eight film samples contained quartz and polypropylene were obtained for one autumn–winter season.

Two high-volume samplers (TH-150C, Tianhong Instrument Co. Ltd., Wuhan, China) were used to collect PM$_{2.5}$ samples. Before the sampling process, the samplers were calibrated, the flow-rate range of the samplers was from 60 to 150 L/min (prolongable), with an accuracy of ±2.5%, and the relative error of the flow-rate of less than 2%. In this sampling process, the flow rate was set as 100 L·min$^{-1}$; quartz and polypropylene
films were loaded to capture PM$_{2.5}$. After sampling, the filter samples were placed in the refrigerator at $-4^\circ$C for preservation.

2.1.2. Quality Assurance and Quality Control of Sampling

The quartz films were first calcined at 450 $^\circ$C for 5 h in order to remove the organics and other impurities on the films. And then, the films were packed into aluminum foil papers and placed in a constant temperature and humidity chamber of 25 $^\circ$C and 50 $\pm$ 5% relative humidity for 24 h. Then the films were sealed in film boxes at the temperature of $-20^\circ$C. Three blank films were reserved as the blank samples to correct the data of each sample in order to guarantee the accuracy and reliability of the analyzed data of the collected samples.

2.2. Chemical Components Analysis

2.2.1. Water Soluble Ions

Before analysis, polypropylene films were extracted ultrasonically by 20 mL of ultra-pure water for 20 min, and then water-soluble matters were filtrated and stored at 4 $^\circ$C. Ion chromatography (Universal ics-90, Swiss) was used to analyze the inorganic ions, which included chloride (Cl$^-$), nitrate (NO$_3^-$) and sulfate (SO$_4^{2-}$), sodium (Na$^+$), ammonium (NH$_4^+$), potassium (K$^+$), magnesium (Mg$^{2+}$), calcium (Ca$^{2+}$), and fluoride (F$^-$).

2.2.2. Carbonaceous Species

A circular quartz filter with an area of 0.558 cm$^2$ was used to determine organic carbon (OC) and elemental carbon (EC) concentrations by a thermal/optical carbon analyzer (Model 2008; Desert Research Institute, Reno, Nevada USA).

The background contamination was regularly monitored by blank tests, which were used to validate and correct the corresponding data. Calibration of the analyzer was done before and after sample analysis every day. The first sample was analyzed every ten samples again, and the precision should be less than 5%.

2.2.3. Inorganic Element

After the digestion process, metal components, such as Li, Be, Mg, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Se, Mo, Cd, Sn, Sb, Ba, Hg, Pb, Bi, Ca, K, Mg, Na, were determined using Inductively Coupled Plasma-Mass Spectrometry (7700 Series ICP-MS, Agilent Technologies Inc., PaloAlto CA, USA). In addition, the concentrations of Al and Si were determined by Inductively Coupled Plasma Atomic Emission Spectrometry (8300 ICP-AES, PerkinElmer company, Boston, Massachusetts, USA).

2.3. Data Analysis Method

2.3.1. Online Data Source

Air quality data were obtained from China’s air quality online monitoring and analysis platform (http://www/aqistudy.cn/historydata, accessed on 27 February 2021), and meteorological data were obtained from the National Oceanic and Atmospheric Administration (ftp://arlftp.arlhq.noaa.gov/pub/archives/gdas1/, accessed on 27 February 2021) which are all open-source database for research.

2.3.2. Analysis of Secondary Pollution

The secondary formation is an important reason for PM$_{2.5}$ pollution. Sulfate and nitrate are the main productions by the secondary formation in PM$_{2.5}$, and the components of which are related to the oxidation efficiency of SO$_2$ and NO$_2$. Usually, the secondary formation rates of SO$_2$ and NO$_2$ are characterized by SOR (sulfate oxidation rate) and NOR (nitrate oxidation rate), which can be calculated by the following equations:

$$\text{SOR} = \frac{(\text{SO}_4^{2-})}{((\text{SO}_4^{2-}) + (\text{SO}_2))}$$  \hspace{1cm} (1)
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\[
\text{NOR} = \frac{(\text{NO}_3^-)}{((\text{NO}_3^-) + (\text{NO}_2))}
\]  

(2)

where (SO$_4^{2-}$) and (NO$_3^-$) are concentrations in PM$_{2.5}$, $\mu$g/m$^3$; (SO$_2$) and (NO$_2$) are the concentrations of the gas phase, $\mu$g/m$^3$.

Secondary organic carbon in the atmosphere is formed by photochemical reactions or gas-particle conversion of volatile and semi-volatile organic compounds. The degree of secondary carbon pollution can be characterized by indicators such as OC/EC and SOC/OC. The higher the ratio represents, the more serious secondary pollution. The secondary OC (SOC) concentrations were determined by the EC tracer method following Equations (3) and (4).

\[
\text{POC} = \text{EC} \times (\text{OC}/\text{EC})_{\text{min}}
\]  

(3)

\[
\text{SOC} = \text{OC} - \text{POC}
\]  

(4)

where POC, SOC, and OC represent the estimated primary OC, secondary OC, and measured total OC, respectively. \((\text{OC}/\text{EC})_{\text{min}}\) is the minimum OC/EC ratio in each sampling period.

Moreover, the value of the OC/EC ratio can also reflect the different combustion emission sources. It was suggested by the studies, the OC/EC ratio of vehicle exhaust emissions is 2.5–5.0, coal combustion is 5.0–10.5, wood-burning is 16.8–40.0, biomass burning is 7.7 [26–28].

2.3.3. Back Trajectory and Clustering Analysis

The 48 h backward trajectories of air mass during the pollution processes were investigated by the Hybrid Single Particle Lagrangian Integrated Trajectory (HYSPLIT) (http://ready.arl.noaa.gov/HYSPLIT.php, accessed on 27 February 2021) model developed by the National Oceanic and Atmosphere Administration (NOAA). The model started at a height of 100 m above ground level (AGL) with a time interval of one hour. Based on the results of the backward trajectory analysis, the trajectories and pollution concentrations were used to cluster analysis by MeteoInfoMap, which is an open-source geographic information system and scientific computing environment software.

Cluster analysis is an objective classification method to study multiple elements (or variables). It looks for a statistical quantity that can objectively reflect the distance relationship between samples and then divides samples into several categories according to the statistical quantity. The clustering method based on airflow trajectory is to group a large number of airflow tracks according to their spatial similarity (transmission velocity and direction). In this study, the Angle Distance algorithm provided by TrajStat software was used to cluster the airflow trajectory, and total spatial variance (TSV) was used to judge the classification quality. The principle is as follows: the TSV of the first several classification steps increases rapidly and then increases slowly. When the categories are divided to a certain number, TSV increases rapidly again, indicating that the merged categories are different. The classification merger is over, and the categories before the merger are the classification results. The average trajectories of these categories are the main flow trajectories of the target point in the analysis periods.

3. Results and Discussion

3.1. Mass Concentrations and Chemical Compositions of PM$_{2.5}$

3.1.1. The Mean Values of Pollutants in the Two Autumn–Winter Seasons

The mean concentrations of PM$_{2.5}$ and its major chemical components of the three sampling sites at Xingtai in the autumn–winter seasons of 2017–2018 and 2018–2019 are presented in Table 1, and the concentrations of other online air pollutants are also shown in this table. The mean concentrations of PM$_{2.5}$, NO$_2$, SO$_2$, and O$_3$ were 125.0, 60, 32, and 51 $\mu$g/m$^3$ in the autumn–winter season of 2017–2018 and those were 112.1, 64, 31, and 40 $\mu$g/m$^3$ in that of 2018–2019. Compared to the autumn–winter season of 2017–2018, the concentrations of PM$_{2.5}$ and SO$_2$ in that of 2018–2019 had a slight decrease. However, the concentrations of NO$_2$ and O$_3$ had a little increase. The air quality index (AQI) of the
two autumn–winter seasons are shown in Figure 2, which shows that the study periods were dominated by polluted weather, specifically, the weather with AQI above 100 (light pollution) accounted for 65.7% and 64.8% in the two autumn-winter seasons, respectively.

Table 1. Mean concentrations and major chemical components of PM$_{2.5}$, and the concentrations of the gaseous pollutants of autumn–winter seasons at Xingtai (µg/m$^3$).

|          | 2017–2018 |          | 2018–2019 |
|----------|-----------|----------|-----------|
|          | YZ | NQ | SH | Average | YZ | NQ | SH | Average |
| NO$_3^-$ | 21.8 | 19.3 | 20.9 | 20.7 | 20.7 | 18.8 | 20.6 | 20.4 | 20.0 |
| SO$_2^{2-}$ | 11.8 | 10.9 | 12.8 | 11.8 | 9.0 | 10.6 | 9.3 | 9.6 |
| NH$_4^+$ | 11.7 | 11.0 | 12.6 | 11.8 | 8.7 | 9.0 | 9.7 | 9.1 |
| K$^+$ | 1.2 | 1.3 | 1.5 | 1.3 | 0.7 | 1.0 | 0.7 | 0.8 |
| Ca$^{2+}$ | 1.9 | 1.4 | 1.6 | 1.6 | 1.5 | 1.5 | 1.7 | 1.6 |
| Cl$^-$ | 4.4 | 4.3 | 6.3 | 5.0 | 3.5 | 4.7 | 3.7 | 4.0 |
| OC | 17.5 | 16.3 | 20.4 | 18.1 | 15.3 | 21.8 | 20.0 | 19.0 |
| EC | 7.5 | 8.5 | 9.8 | 8.6 | 6.9 | 8.4 | 7.1 | 7.5 |
| PM$_{2.5}$ | 121.8 | 117.1 | 136.2 | 125.0 | 105.1 | 112.1 | 119.1 | 112.1 |

$^1$ The concentrations of NO$_2$, SO$_2$, and O$_3$ were obtained from the China air quality online monitoring and analysis platform (http://www/aqistudy.cn/historydata, accessed on 27 February 2021).

Water-soluble inorganic ions are important components of PM$_{2.5}$ which mainly include NO$_3^-$, SO$_2^{2-}$, NH$_4^+$, K$^+$, Ca$^{2+}$, and Cl$^-$ [29,30]. These inorganic ions play an important role in the formation of PM$_{2.5}$. On average, the most abundant water-soluble species in PM$_{2.5}$ were ranked as follows: NO$_3^-$ (20.7 µg/m$^3$), SO$_2^{2-}$ (11.8 µg/m$^3$), NH$_4^+$ (11.8 µg/m$^3$), Cl$^-$ (5.0 µg/m$^3$), Ca$^{2+}$ (1.6 µg/m$^3$), and K$^+$ (1.3 µg/m$^3$) in 2017–2018, and NO$_3^-$ (20.0 µg/m$^3$), SO$_2^{2-}$ (9.6 µg/m$^3$), NH$_4^+$ (9.1 µg/m$^3$), Cl$^-$ (4.0 µg/m$^3$), Ca$^{2+}$ (1.6 µg/m$^3$), and K$^+$ (0.8 µg/m$^3$) in 2018–2019. Mean concentrations of SNA (Secondary inorganic aerosol, which is the sum of SO$_2^{2-}$, NO$_3^-$, and NH$_4^+$) were 44.3 µg/m$^3$ in 2017–2018 and 38.7 µg/m$^3$ in 2018–2019, contributing 35.4% and 34.5% in PM$_{2.5}$ mass. It can be concluded that in two autumn–winter seasons, the mass concentration values of SO$_2^{2-}$ and NH$_4^+$ were all similar, which suggested that (NH$_4$)$_2$SO$_4$ was the main formation of SO$_2^{2-}$ and NH$_4^+$ in PM$_{2.5}$. Furthermore, it also can be seen that the mass concentration of NO$_3^-$ was more than that of SO$_2^{2-}$, which suggests that the pollution style of Xingtai was of nitrate, indicating that the usage control of carbon reduced SO$_2$ emissions effectively, however, NO$_x$ emissions of vehicles and gas-fired boilers should be controlled further.

Carbonaceous species, which mainly include EC and OC, were found to contribute significantly to the formation of fine particles. EC is one of the main light-absorbing species in fine particles and also is the gas to particle reaction medium for SO$_2$ and NO$_x$ [31].
Moreover, EC is a good indicator of primary anthropogenic pollutants [28]. The source of OC is more complex. Besides the primary emissions from industrial production, fuel combustion, and natural sources, there is secondary organic carbon (SOC) produced by photochemical reactions of gaseous precursors in the atmosphere [32]. The mean concentrations of OC and EC were 26.6 and 18.1 µg/m³ in the autumn–winter season of 2017–2018, and those were 19.0 and 7.5 µg/m³ in that of 2018–2019. The contributions of OC and EC in the PM_{2.5} mass concentrations were 21.3% and 18.1% in the autumn–winter season of 2017–2018, and those were 16.9% and 6.7% in that of 2018–2019. The concentration and ratio of EC all had an obvious decline in 2018–2019 compared with 2017–2018 in the study period, suggesting that the direct emission of fossil fuel and incomplete combustion of biomass from pollution sources [33] were reducing. It was known that the plan of Xingtai’s comprehensive control of air pollution had been issued, which controlled the scattered coal burning for civil use effectively. The measures of the plan included a ban on burning scattered coal, connecting the urban heating network, carrying out central heating or clean heating in all county areas. Through these measures, control of the combustion of scattered coal at Xingtai in the autumn-winter season of 2018–2019 achieved initial success.

Usually, the OC/EC values are often used to determine whether secondary pollution occurs. If the OC/EC values exceed 2.0, there is secondary pollution [34]. Through calculation, the average OC/EC value in the autumn–winter season of 2017–2018 was 2.1, and that of 2018–2019 was 2.3. Therefore, secondary pollution more likely happened in the autumn–winter season of 2017–2018 and 2018–2019. Moreover, the concentrations of SOC could also reflect the level of secondary pollution and were also calculated. The concentration of SOC were 1.3 and 6.9 µg/m³ in the study period of 2017–2018 and 2018–2019, respectively, accounting for 4.9% and 38.1% in OC, respectively, suggesting that the chemical conversion process had more effects on the formation of PM_{2.5} in the autumn–winter season of 2018–2019 compared that of 2017–2018. On the other side, it could also be concluded that the atmospheric oxidation of 2018–2019 was higher than that of 2017–2018 at Xingtai.

In this study, the OC/EC ratios were 2.1 and 2.3 in the autumn–winter season of 2017–2018 and 2018–2019, respectively. Thus, the main combustion source was vehicle exhaust. OC/EC ratios of 2018–2019 have increased which were attributed to the increase in atmospheric oxidation. NOx was the main oxidizing substance in the atmosphere, and NOx released by vehicle emissions contributed significantly, so more efforts should be directed toward vehicle NOx emissions.

3.1.2. The Mean Values of the Three Sampling Sites in the Autumn–Winter Seasons

Table 1 shows the mass concentrations of PM_{2.5} and its major chemical components in the three monitoring stations. Neiqiu and Shahe are two counties located in the upwind and downwind directions of the main urban city of Xingtai during the autumn–winter season. Among the three sampling sites, Shahe is an important industry county, which had many glass, ceramics, and coking industries. In general, as seen in Table 1, compared to the year 2017–2018, the mass concentration of PM_{2.5} in the three sampling sites of YZ, NQ, and SH all decreased by 13.7%, 4.3%, and 12.6%, respectively, in the year 2018–2019. However, both in the two autumn–winter seasons, the mass concentration of PM_{2.5} in SH was the highest, which could be attributed to more agminated factories.

Table 1 also shows that all the PM_{2.5} components have a similar pattern. The average concentrations of the total water-soluble ions at YZ, NQ, and SH were 52.7, 48.3, and 55.6 µg/m³ in the autumn–winter season of 2017–2018, and those were 42.2, 47.4, and 45.5 µg/m³ in that of 2018–2019, the decrease ratios were 19.9%, 1.9%, and 18.2%, respectively. Moreover, the decreasing rates of ion concentrations were calculated, as for SNA, and the decrease ratios of YZ and SH were all larger than those of NQ. It can be speculated that NQ was easily affected by the pollution transport. Moreover, it was to note that the concentration of NO_3^- was increased at NQ, which all suggested that nitrate pollution was a severe air pollution issue.
As seen in Table 1, the concentrations of OC in the three sampling sites were 17.5, 16.3, and 20.4 µg/m³ in the autumn–winter season of 2017–2018 and those were 15.3, 21.8, and 20.0 µg/m³ in 2018–2019. Compared to the autumn–winter season of 2017–2018, OC and EC values of YZ and SH all had a slight decrease in that of 2018–2019. However, as for NQ, OC value was increased, and EC value kept steady. It could be concluded that in autumn–winter seasons, the additional fossil fuels clearly lead to an increase in OC emissions, and under the unfavorable meteorological conditions, the higher concentrations of OC may be precursors and attributed to the increase in secondary formations [35,36].

The mass concentrations of Cl⁻, K⁺, and Ca²⁺ were relatively low in the total water-soluble inorganic ions. K⁺ could be used to trace biomass emissions and fireworks emissions [37]. It was suggested that the mass concentration of K⁺ in the autumn–winter season of 2018–2019 was lower than that of 2017–2018. It was known that the Administrative Measures of Xingtai City on Banning Open Burning (Trial) was released in 2018–2019, and biomass burning has been further controlled effectively so that the mass concentration of K⁺ of the three sampling sites all had decreased. Chloride ions (Cl⁻) mainly come from coal combustion [38], and the mass concentrations of Cl⁻ in YZ and SH all decreased in the autumn–winter season of 2017–2018 compared to those of 2018–2019, suggesting that the coal-fired combustion was further controlled in 2018–2019 compared to 2017–2018. Calcium ions (Ca²⁺) mainly come from crustal-derived ions and are indicators of soil-related sources [39]. As shown in Table 1, the concentration of Ca²⁺ in the two autumn–winter seasons were similar, suggesting that those seasons suffered a similar sandstorm situation.

### 3.2. Chemical Components Analysis at Different PM₂.₅ Concentration Levels

Among the normal six-item air pollutants, CO is not an active photochemical and has a chemical life of about several months. In a short period, CO can be regarded as an inert pollution tracer, mainly controlled by meteorological parameters [40–43]. The ratios of PM₂.₅/CO, SO₂/CO, NO₂/CO, and O₃/CO were calculated under different AQI levels to understand the relative contribution of the chemical processes to PM₂.₅.

It can be seen in Table 2, the concentration ratios of PM₂.₅/CO and SO₂/CO did not change obviously with different PM₂.₅ concentration levels in both years. However, the ratio of NO₂/CO and O₃/CO all decreased with an increase in PM₂.₅ concentration levels, suggesting that on heavy pollution days, the chemical conversion processes of the pollutants happened. NO₂ acted as reactants to produce the chemical reactions and forming more sulfates and nitrates, and O₃ formation process was restrained. It can be seen in Table 2 that the concentration ratio of O₃/CO had an obvious decrease with the increase in the concentration ratio of PM₂.₅/CO. Thus, it can be speculated that on heavy pollution days, the concentration of PM₂.₅ and O₃ had a negative correlation because of the chemical conversion processes, and O₃ could act as an important oxidizing agent. On the other hand, photochemical production of O₃ decreased during the occurrences of haze events which also attribute to the decrease in O₃/CO.

| PM₂.₅ Concentration Levels | PM₂.₅/CO 2017–2018 | PM₂.₅/CO 2018–2019 | SO₂/CO 2017–2018 | SO₂/CO 2018–2019 | NO₂/CO 2017–2018 | NO₂/CO 2018–2019 | O₃/CO 2017–2018 | O₃/CO 2018–2019 |
|---------------------------|------------------|------------------|------------------|------------------|------------------|------------------|------------------|------------------|
| <50                       | 54               | 60               | 15               | 17               | 34               | 38               | 30               | 33               |
| (50,100)                  | 45               | 54               | 16               | 19               | 31               | 43               | 32               | 38               |
| (100,150)                 | 45               | 52               | 15               | 19               | 30               | 40               | 22               | 25               |
| (150,200)                 | 41               | 47               | 15               | 18               | 25               | 36               | 26               | 22               |
| >200                      | 57               | 44               | 19               | 21               | 29               | 35               | 25               | 24               |

In order to analyze the chemical components of PM₂.₅ at different pollution levels, in this study, we further split the days into five levels according to the concentration of PM₂.₅ as shown in Figure 3. The columns presented the average concentrations of PM₂.₅.
at their respective pollution levels. It can be seen in Figure 3, the concentration of Ca$^{2+}$ and K$^+$ are at low levels, suggesting that sand storms and biomass burning had fewer contributions to the concentration of PM$_{2.5}$. The concentration of Cl$^-$ stays stable with the increase in pollution level, indicating that the contribution of coal combustion to the air pollution did not further increase with the deepening of the pollution. It is to note in Figure 3, the concentration variation trends of SO$_4^{2-}$ and NH$_4^+$ were similar, which increase with the increase in PM$_{2.5}$ concentration. It was indicated that (NH$_4$)$_2$SO$_4$ was the important component of PM$_{2.5}$. Considering that SO$_4^{2-}$ also mainly come from coal combustion, the emission level of coal combustion did not increase due to the stable level of Cl$^-$ concentration. Thus, it could be concluded that the atmospheric oxidation increased with the deepening of pollution and making the secondary conversion level increase. NO$_3^-$ was the main water-soluble ion of PM$_{2.5}$, and the pollution style of the autumn–winter season in Xingtai was nitrate dominant. Moreover, the concentration of NO$_3^-$ increased sharply when the concentration of PM$_{2.5}$ was higher than 150 $\mu$g/m$^3$, which also proved that the secondary conversion process was enhanced at the heavy pollution weather.

![Figure 3](image-url)

**Figure 3.** Concentration of water-soluble ions at different concentration levels of PM$_{2.5}$.

The concentrations of EC, OC, and the concentration ratios of OC/EC, NO$_3^-$/SO$_4^{2-}$ at different concentration levels of PM$_{2.5}$ in the two autumn–winter seasons are shown in Figure 4. With the increase in the PM$_{2.5}$ concentration levels, the concentrations of OC and EC all increased. Though the concentrations of OC and EC in the autumn–winter season of 2018–2019 were lower than those of 2017–2018, the concentration ratio of OC/EC in 2018–2019 was higher than that in 2017–2018, indicating that though the total carbon decreased, the secondary conversion rate increased. OC/EC level was higher at the high concentration level of PM$_{2.5}$, suggesting that chemical conversion was enhanced during high pollution weather. The concentration ratios of NO$_3^-$/SO$_4^{2-}$ are also shown in Figure 4, which indicates that the concentration ratios of NO$_3^-$/SO$_4^{2-}$ in the autumn–winter season of 2018–2019 were higher than those of 2017–2018, which also proves the importance of NO$_x$ pollution control.
3.3. Impacts of Meteorological Parameters and Secondary Formation

Fine particulate matter (PM$_{2.5}$) and O$_3$ are the main substances causing air pollution in China, and it was testified that the combined pollution of PM$_{2.5}$ and O$_3$ were affected by the meteorological parameters and secondary formation [43–45].

3.3.1. Impacts of Meteorological Parameters on the Formation of PM$_{2.5}$ and O$_3$

The online concentrations of PM$_{2.5}$ and O$_3$ in the two autumn–winter seasons are shown in Figure 5, the average online concentration of PM$_{2.5}$ and O$_3$ were 100 and 51 µg/m$^3$ at the autumn–winter season of 2017–2018, and those were 100 and 40 µg/m$^3$ in the autumn–winter season of 2018–2019. Thus, it could be concluded that PM$_{2.5}$ was the main air pollutant in the autumn–winter season in Xingtai. As shown in Figure 5, the concentrations of PM$_{2.5}$ and O$_3$ had different variation tendencies. Thus, it is speculated that the meteorological parameters and secondary formation had different effects on the formation of PM$_{2.5}$ and O$_3$.

The meteorological parameters of the two autumn–winter seasons are shown in Figure 6. The average wind speed, temperature, and relative humidity were 3.0 m/s, 4 °C, and 49.9% in the autumn–winter season of 2017–2018, and those were 2.9 m/s, 4 °C, and 47.7% in the autumn–winter season of 2018–2019. Thus, it could be concluded that the meteorological conditions of the two autumn–winter seasons were similar, which all had low wind speed and high relative humidity. It could be concluded from Figure 6, high humidity and low wind speed could promote the formation of air pollution. It was because in the autumn–winter seasons, low temperature and low wind speed caused the accumulation of pollution. Moreover, the high relative humidity increased the reaction rate of the heterogeneous and liquid phase reactions, which was in favor of the pollution process. In addition, it also can be seen in Figure 6, that wind has obvious effects on removing pollution.
Figure 5. Concentration of PM$_{2.5}$ and O$_3$-8h at the autumn–winter seasons of 2017–2018 (a) and 2018–2019 (b).

Figure 6. The diagram variations of meteorological parameters and concentration of PM$_{2.5}$ at the autumn–winter seasons of 2017–2018 (a) and 2018–2019 (b).
In order to explore the correlations between the concentrations of PM\(_{2.5}\), O\(_3\), and the meteorological parameters, Kendall’s Tau coefficients were calculated, and the calculation results are shown in Table 3. It can be seen in Table 3, both PM\(_{2.5}\) and O\(_3\) had a weak correlation with the average air pressure. It can be seen that wind speed had a positive correlation with the concentration of O\(_3\) and had a negative correlation with the concentration of PM\(_{2.5}\). Thus, it is suggested that wind had the opposite effects on the formation of PM\(_{2.5}\) and O\(_3\). The formation of O\(_3\) mainly depended on the secondary formation of the emission pollutants, and it was speculated that wind could increase the disturbance of the chemical matters in the atmosphere, further increase the reactants contacting probability of O\(_3\). As for PM\(_{2.5}\), nucleation is the main step for the formation of PM\(_{2.5}\). However, high wind speed increases the disturbance of airflow, inhibiting the forming of the nucleus.

Table 3. Kendall’s tau coefficient between pollution concentrations and meteorological.

| Year     | Pollutant | Average Air Pressure | Average Wind Speed of 2 Min | Average Temperature | Average Relative Humidity |
|----------|-----------|----------------------|----------------------------|---------------------|--------------------------|
| 2017–2018 | PM\(_{2.5}\) | −0.137               | −0.163                     | −0.097              | 0.165                    |
|          | O\(_3\)   | −0.075               | 0.135                      | 0.340               | −0.027                   |
| 2018–2019 | PM\(_{2.5}\) | 0.018                | −0.123                     | −0.229              | 0.221                    |
|          | O\(_3\)   | −0.210               | 0.267                      | 0.487               | −0.078                   |

It also can be seen in Table 3, the temperature had a higher Kendall’s Tau coefficient with the concentration of O\(_3\) than that of PM\(_{2.5}\), suggesting that O\(_3\) is affected more easily by temperature. Higher temperatures were beneficial for the photochemical reaction to form O\(_3\), and went against the coagulating effects for forming PM\(_{2.5}\). The average relative humidity also had a positive correlation with the concentration of PM\(_{2.5}\), which demonstrated that water played an important role in the formation of PM\(_{2.5}\), because water molecules are an important component in the nucleation process.

3.3.2. The Influence Factor of Secondary Aerosols in the Autumn–Winter Seasons

NOR and SOR are the indicators of secondary aerosols in the atmosphere. The average values of NOR and SOR were 0.22 and 0.27 in the autumn–winter season of 2017–2018 and those were 0.23 and 0.20 in that of 2018–2019, and the values of NOR in the two autumn–winter seasons were similar, the value of SOR was higher in the autumn–winter season of 2017–2018 compared to that of 2018–2019. According to Table 3, the temperature and relative humidity have more effects on the formation of PM\(_{2.5}\) and O\(_3\), thus in order to study the relationships between the secondary aerosols and PM\(_{2.5}\) concentration, O\(_3\) concentration, relative humidity, and temperature, the correlations of them at the two autumn-winter seasons are shown in Figures 7 and 8, respectively. Kendall’s tau coefficient between NOR, SOR, and the temperature, relative humidity concentration of PM\(_{2.5}\), O\(_3\) are shown in Table 4.

Table 4. Kendall’s tau coefficient between NOR, SOR, and the temperature, relative humidity concentration of PM\(_{2.5}\), O\(_3\).

| Year     | Pollutant | PM\(_{2.5}\) | O\(_3\) | Average Relative Humidity | Average Temperature |
|----------|-----------|-------------|--------|---------------------------|---------------------|
| 2017–2018 | NOR       | 0.440       | −0.101 | 0.579                     | 0.139               |
|          | SOR       | 0.295       | 0.082  | 0.593                     | 0.214               |
| 2018–2019 | NOR       | 0.252       | −0.076 | 0.372                     | 0.090               |
|          | SOR       | 0.205       | −0.032 | 0.540                     | 0.209               |
As shown in Figures 7 and 8, the relationships of NOR and SOR against the temperature present a “U” shape. The values of NOR and SOR show small values at a temperature around 4 °C. It was speculated that the oxidation processes of SO$_2$ and NO$_2$ could be conducted either in the gaseous phase of the atmosphere or the interface between the gas phase and particle phase of the nuclei, and higher temperature benefited oxidation reaction in the gas phase. However, lower temperature benefited the nucleation process of the pollutants in the atmosphere, which provided larger surface areas for the inter-phase oxidation reactions. Thus, when the temperature was around 4 °C, gas-phase oxidation and gas-solid-phase oxidation were also not promoted, and NOR and SOR were relatively low.

It can be seen in Figures 7 and 8, the relative humidity (RH) plays an important role in the formation of nitrates and sulfates. Thus, NOR and SOR increase with the increase in RH. It was suggested by the previous studies, RH could promote the formation of NO$_3^-$ and SO$_4^{2-}$ in two ways: one way was that original sulfate and nitrate could adsorb water to enlarge the particles’ surfaces, and larger particle surfaces also promote the
heterogeneous reaction to form NO$_3^-$ and SO$_4^{2-}$; the other way was that higher RH could decrease the viscosity of the surface of the particles, which increased the conversion rate of gas precursors to particulate matter kinetically, resulting in more pollutant converting to particulate state, which promotes heterogeneous reactions [46].

By calculation, Kendall’s tau coefficients were 0.440 and 0.295 for NOR and SOR to the concentration of PM$_{2.5}$, respectively in the autumn–winter season of 2017–2018, and those were 0.252 and 0.205 in that of 2018–2019 (As seen in Table 4). NOR and SOR showed a positive correlation with the concentration of PM$_{2.5}$, indicating that the secondary formation contributes to the formation of PM$_{2.5}$, and the promotion effects were not very strong, which suggested that except for the secondary formation, many other factors all affected the formation of PM$_{2.5}$ pollution. The Kendall’s tau coefficients were $-0.101$ and $0.082$ for NOR and SOR to the concentration of O$_3$, respectively in the autumn–winter season of 2017–2018, and those were $-0.076$ and $-0.032$ in the autumn–winter season of 2018–2019. It could be concluded that the concentration of O$_3$ had a poor correlation with NOR and SOR. Thus, it was speculated the secondary formation process of SO$_4^{2-}$ and NO$_3^-$ had minor effects on the formation of O$_3$. The photochemical reaction of O$_3$ and secondary formation of SO$_4^{2-}$, NO$_3^-$ may be controlled by different main factors. Humidity and temperature had a positive effect on the formation of SOR and NOR. It was suggested that higher temperatures and a humid environment could accelerate the chemical reaction.

3.4. Identification of Potential Transported Sources

Regional transport is another important reason for the formation of air pollution. Thus, the meteorological conditions and transport of PM$_{2.5}$ and O$_3$ during the pollution processes were studied. As shown in Table 5, there were six pollution processes during the sampling periods in 2017–2018, and the information on the pollution processes is shown in Table 5.

Table 5. Information of pollution processes at the autumn-winter season of 2017–2018.

| No. | Pollution Times (Month/Day) | Duration Times | Concentration of PM$_{2.5}$($\mu$g/m$^3$) | Pollution Level |
|-----|----------------------------|----------------|------------------------------------------|-----------------|
| I   | 10/25–10/28                | 4 days         | Average value: 140.3 $\mu$g/m$^3$  
Peak value: 196 $\mu$g/m$^3$ | medium pollution: 2 days  
heavy pollution: 1 day  
light pollution: 1 day |
| II  | 12/1–12/5                 | 5 days         | Average value: 143 $\mu$g/m$^3$  
Peak value: 214 $\mu$g/m$^3$ | heavy pollution: 2 days  
light pollution: 1 day |
| III | 12/12–12/15                | 3 days         | Average value: 122 $\mu$g/m$^3$  
Peak value: 179 $\mu$g/m$^3$ | heavy pollution: 1 day  
light pollution: 1 day  
light pollution: 5 days |
| IV  | 12/25–1/2                 | 9 days         | Average value: 132 $\mu$g/m$^3$  
Peak value: 251 $\mu$g/m$^3$ | heavy pollution: 2 days  
sever pollution: 1 day  
light pollution: 3 days |
| V   | 1/12–1/22                 | 10 days        | Average value: 176 $\mu$g/m$^3$  
Peak value: 286 $\mu$g/m$^3$ | medium pollution: 1 day  
heavy pollution: 4 days  
sever pollution: 2 days  
light pollution: 2 days  |
| VI  | 1/27–1/30                 | 4 days         | Average value: 135 $\mu$g/m$^3$  
Peak value: 209 $\mu$g/m$^3$ | medium pollution: 1 day  
light pollution: 2 days |

The wind roses of the six pollution periods and the whole sampling period at the autumn–winter season of 2017–2018 are shown in Figure 9. It can be seen in Figure 9A, the predominant wind direction in the autumn–winter season was northwest. However, the predominant wind directions during the pollution periods were southeast and north-east directions, as shown in Figure 9B. Thus, it can be suggested that the pollution of Xingtai is mainly affected by the east cities at Shandong and Hebei province.
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Figure 9. The wind roses of the six pollution periods (A) and the whole sampling period (B) at the autumn–winter season of 2017–2018.

The clustering analysis of the backward flow trajectory of the six typical pollution processes was conducted, and the clustering results are shown in Figure 10. It can be seen that all the pollution processes were affected by the airflow coming from the east. In order to make clear the pollution concentrations in each airflow trajectory, three pollution processes were selected, and the pollutants (O$_3$ and PM$_{2.5}$) contribution ratio is shown in Figure 11. As shown in Figure 11, O$_3$ and PM$_{2.5}$ usually have different main transport paths. The main PM$_{2.5}$ transport paths of the pollution processes I, III, and VI were path 2, path 2, and path 3, respectively; however, the main O$_3$ transport paths of those pollution processes were path 1, path 4, and path 3, respectively. It could be concluded that the main pollution transport paths of O$_3$ in Xingtai were all from the east. Thus, O$_3$ pollution of Xingtai in winter was easily affected by Shandong province except for the Beijing–Tianjin–Hebei area. As seen in Figure 9B, the predominant wind direction in Xingtai is northwest. However, among the main pollution transport paths of the pollutants, only in pollution process I, the main PM$_{2.5}$ pollution was transported from the northwest. Thus, it was suggested that the pollution emissions of the cities located in the east of Xingtai had more effects on the pollution processes of Xingtai. It can be considered that more focus should be paid to the industrial restructuring and energy structure optimization of the cities at the east of Beijing–Tianjin–Hebei area to control PM$_{2.5}$ and O$_3$ pollution synergistically.

Figure 10. The clustering results of the six pollution processes, path 1, path 2, path 3 (1,2,6); path 1, path 2, path 3, path 4, path 5 (3,5); path 1, path 2, path 3, path 4, path 5, path 6 (4).
Xingtai city, located at the south part of the Beijing–Tianjin–Hebei area, east side of the Taihang mountains, which has developed secondary industry leading to large amounts of local emissions. In addition, Xingtai city is affected by the pollution transport obviously, and local pollutants are hard to diffuse, which is a typical industry city with bad pollutant diffusion conditions. This study made a comprehensive analysis of air pollution from the aspects of pollutants emission, meteorology conditions, secondary formation, and pollutants transport, respectively, in two autumn–winter seasons of 2017–2018 and 2018–2019 at Xingtai. Moreover, the effects of the secondary formation and meteorological conditions on the combined pollution of PM$_{2.5}$ and O$_3$ were explored due to the fact that combined pollution controlling was a new challenge in China. The rules of the relationship between PM$_{2.5}$, O$_3$, and other factors were studied, and air trajectories and pollutant concentrations were clustered to find different transmission paths of PM$_{2.5}$ and O$_3$. The specific research conclusions are shown below:

1. PM$_{2.5}$ concentration had a slight decrease in the autumn–winter season of 2018–2019 compared to that of 2017–2018, the concentration of EC, SO$_4^{2-}$, NH$_4^+$, Cl$^-$, and K$^+$ all decreased, which could attribute to carrying out the central and clean heating policies and control of biomass burning policy at Xingtai in 2018–2019. However, the secondary formation rates increased obviously in the autumn–winter season and the concentration of NO$_3^-$ kept steady. In addition, the average concentration of NO$_2$ also increased. Thus, NO$_x$ control was an important pollutant control work in the future.
2. The formation of \( \text{O}_3 \) and \( \text{PM}_{2.5} \) all affected by the secondary formation and meteorological conditions, but the impact effects of the factors were not the same. With the increase in \( \text{PM}_{2.5} \) pollution levels, the secondary formation increased, and \( \text{O}_3 \) was consumed. Furthermore, the study of correlation suggested that the concentrations of \( \text{O}_3 \) and \( \text{PM}_{2.5} \) were easily affected by the temperature and relative humidity, respectively.

3. The increase in the relative humidity benefited the formation of SOR and NOR. The relationships of NOR and SOR against temperature present a “U” shape. The values of NOR and SOR showed small values at a temperature of around 4 °C because gas-phase oxidation and gas-solid-phase oxidation were also not promoted at this temperature, thus decreased the secondary formation.

4. The cluster of air trajectories and concentrations of \( \text{PM}_{2.5} \) and \( \text{O}_3 \) showed that the pollution of Xingtai is mainly affected by the east cities located in the Shandong and Hebei province. The east route was the main transport route for \( \text{O}_3 \) and \( \text{PM}_{2.5} \). However, the concentration of \( \text{PM}_{2.5} \) was also affected by the airflow coming from the northwest.

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