Formation and Evolution of Secondary Particulate Matter During Heavy Haze Pollution Episodes in Northeast China in Winter

Ye Hong (✉ yehongofxf@126.com)

Institute of Atmospheric Environment, CMA, Shenyang <https://orcid.org/0000-0001-8784-3403>

Junying Sun

China Meteorological Administration Chinese Academy of Meteorological Sciences

YanJun Ma

China Meteorological Administration Institute of atmospheric environment Shenyang logy

YangFeng Wang

China Meteorological Administration Institute of Atmospheric Environment, Shenyang

Xiaolan Li

China Meteorological Administration Institute of Atmospheric Environment, Shenyang

Yunhai Zhang

Institute of Atmospheric Environment, CMA, Shenyang

Ningwei Liu

Institute of Atmospheric Environment, CMA, Shenyang

HuJia Zhao

Institute of Atmospheric Environment, CMA, Shenyang

DePing Zhou

Institute of Atmospheric Environment, CMA, Shenyang

Research Article

Keywords: Haze, PM_{2.5}, northeast China, chemical composition, meteorological factors

Posted Date: December 13th, 2021

DOI: <https://doi.org/10.21203/rs.3.rs-987566/v1>

License: © ⓘ This work is licensed under a Creative Commons Attribution 4.0 International License. [Read Full License](#)

Abstract

Based on the simultaneous observation of fine particulate matter ($PM_{2.5}$) and its chemical components in four heavy haze pollution episodes at 14 sampling sites in northeast China from 2017 to 2019, the formation and existence of sulfate (SO_4^{2-}) and nitrate (NO_3^-) secondary contaminants under different stages of the pollution episodes, and different meteorological and emission conditions were compared. The results yielded three main findings. (1) Organic carbon (OC) was the most important component of $PM_{2.5}$, followed by NO_3^- , SO_4^{2-} , and ammonium (NH_4^+). Nitrate surpassed sulfate as the most important secondary inorganic component over the study period. (2) The significant increase in atmospheric OC, SO_4^{2-} , and NO_3^- concentrations was an important reason for haze formation. Meteorological factors such as wind direction, wind speed, temperature (T), relative humidity (RH), and atmospheric oxidability played an important role in secondary pollutant formation. (3) There were two potential SO_4^{2-} formation mechanisms. The first was the gas-phase reaction of the hydroxyl radical ($OH\cdot$) leading to the oxidation of nitrogen dioxide (NO_2) and sulfur dioxide (SO_2), and high ozone (O_3) concentrations. A high atmospheric oxidability and high winter Ts were very important for SO_4^{2-} formation. The second mechanism occurred under neutral or weakly alkaline conditions when large amounts of SO_2 could enter aerosol droplets, and NO_2 was more likely to react in the aqueous phase with SO_2 to increase the output of SO_4^{2-} . Nitrate formation may be mainly due to the homogeneous gas-phase reaction of $OH\cdot$ with NO_2 , SO_2 , and ammonia (NH_3). The highest NO_3^- concentration was observed under mild winter Ts, high RH, high atmospheric oxidability (O_3 and nitrous acid ($HONO$)), high NH_3 concentrations, and suitable light conditions. The differences in SO_4^{2-} formation between northeast China and other regions were mainly a result of the suppression of the aqueous reaction of SO_4^{2-} due to the low T in winter and low-sulfur coal emissions, which resulted in the gas-phase oxidation process with the highest SO_4^{2-} production capacity becoming an important process. However, the aqueous reaction process was the most common mechanism of SO_4^{2-} production in northeast China.

Introduction

There has been an increase in haze pollution in northeast China in recent years. The causes of haze pollution and the formation of the major chemical pollutants are not well understood. Northeast China is located in the mid-high latitudes of the northern hemisphere and is an area with large anthropogenic emissions (van Donkelaar et al., 2016). It is also one of the regions of the world where the terrestrial climate is warming the most rapidly due to global climate change. The rate of increase in the winter surface temperature (T) is significantly higher than the Chinese and global average (Zhao et al., 2007). This change will have an impact on the regional and global climate (Sobhaniet al., 2018). During heavy haze periods in northeast China, aerosols make the most significant contribution to organic carbon (OC) and secondary inorganic components (e.g., sulfate (SO_4^{2-}) and nitrate (NO_3^-)) in the atmosphere (Li et al., 2019). Both can account for more than 50% of fine particulate matter ($PM_{2.5}$) and play a pivotal role in haze formation (Zhang et al., 2020). Therefore, clarifying the causes of secondary aerosol formation is the key to understanding the causes of the persistent heavy haze in this region.

The occurrence of haze pollution is closely related to the chemical reactions between polluted particles in the air. Various physical processes and chemical reactions occur between different ions under different meteorological conditions, which strengthens the photochemical effect of haze particles and is the internal promoting factor of the "explosive" nature and "sustainability" of strong haze pollution (Wang et al., 2014). Sulfate in the atmosphere is mainly formed by the photochemical oxidation of sulfur dioxide (SO_2), which can be formed either by gas-phase homogeneous reactions or aqueous heterogeneous oxidation reactions. Studies have shown that the gas-phase oxidation is mainly the gas-phase oxidation of SO_2 by the hydroxyl radical ($OH\cdot$), and aqueous oxidation occurs mainly in cloud/fog water droplets or aerosols, under the catalysis of transition metal ions (TMs), e.g., Fe(III) and Mn(II), the oxidation of S(IV) by hydrogen peroxide (H_2O_2), ozone (O_3), organic peroxides and oxygen (O_2), of which aqueous oxidation is the main SO_4^{2-} formation pathway worldwide (Wang et al., 2021). Its generation rate is closely related to the pH of the particulate matter. Under acidic conditions, the catalytic oxidation of transition metals accounts for more than 90% of the generation, while under near-neutral conditions, the oxidation of H_2O_2 and nitrogen dioxide (NO_2) each account for 50% (Wang, 2021a). A typical feature of the heavy pollution in northern China in winter is a rapid increase in the SO_4^{2-} concentration, and the sulfur oxidation rate increases exponentially with an increase in the relative humidity (RH) (Elser et al., 2016). This indicates that the heterogeneous chemical reaction under a high RH is an important pathway for SO_4^{2-} formation during heavy haze pollution episodes (Zheng et al., 2015). Through a smoke box simulation study, Wang (2016a) found that the liquid (aqueous) phase oxidation of SO_2 by NO_2 on $PM_{2.5}$ in China's atmosphere is an important SO_4^{2-} formation mechanism during haze periods in China. The Ge research group has reported (Wang et al., 2021b) that the SO_4^{2-} formation mechanism in eastern China in winter is mainly due to the rapid catalytic oxidation of SO_2 by manganese (Mn) ions on the surface of aerosols under low T and high RH conditions. The high ionic strength of the aerosol greatly enhances this reaction. The reaction rate is two to three orders of magnitude higher than that of the traditional aqueous reaction, which can explain 92.5% of the SO_4^{2-} formation. Meteorological factors are very important for haze formation. Sun et al. (2016) used aerosol mass spectrometry to study the generation and elimination mechanisms of typical heavy haze pollution. It is believed that the synergistic influence of meteorology and chemistry is the key to the generation and elimination of haze. Static and stable meteorological conditions, high pollution emissions and rapid secondary aerosol formation are important factors in haze formation, especially the proportion of secondary particles during periods of heavy pollution, which can account for as much 70% of all atmospheric particles. Han et al. (2018) showed that secondary SO_4^{2-} formation on polluted days had a strong

correlation with the effect of NO_2 on SO_2 oxidation, while the oxidation effect of O_3 was less important. Liu et al. (2015) also pointed out that meteorological factors, oxidants, and pH had an important influence on the formation of secondary NO_3^- and SO_4^{2-} .

Nitrate in the atmosphere is mainly derived from the photochemical generation of NO_2 and $\text{OH}\cdot$ during the day and the heterogeneous hydrolysis of dinitrogen pentoxide (N_2O_5) at night (Seinfeld, 2006). In recent years, the proportion of NO_3^- in $\text{PM}_{2.5}$ during heavy pollution periods in China and the ratio of the NO_3^- and SO_4^{2-} concentrations has been constantly increasing. Recent studies have shown that NO_3^- formation is mainly driven by the gas-phase oxidation of NO_x . The oxidation of $\text{OH}\cdot$ during the daytime contributes about 70–90% of atmospheric NO_3^- , and the oxidation of nitro radicals at nighttime contributes about 10–30%. Due to the enhanced uptake of NO_3^- + volatile organic compounds (VOCs) and N_2O_5 , NO_3^- particle pollution has continued to increase in recent years and has exceeded that of SO_4^{2-} (Wang, 2021b). Luo et al. (2020) reported that the level of $\text{PM}_{2.5}$ pollution has an impact on the atmospheric accumulation of NO_3^- . In the cold season, when the $\text{PM}_{2.5}$ concentration is less than $100\text{ }\mu\text{g m}^{-3}$, with an increase in the $\text{PM}_{2.5}$ concentration, the NO_3^- formation pathway gradually shifts from $\text{NO}_2 + \text{OH}\cdot$ to $\text{N}_2\text{O}_5 + \text{H}_2\text{O}$ and $\text{NO}_3 + \text{VOCs}$. When the $\text{PM}_{2.5}$ concentration is greater than $100\text{ }\mu\text{g m}^{-3}$, the NO_3^- formation pathway remains unchanged ($\text{NO}_2 + \text{OH}\cdot$).

In recent years, studies of the chemical components in atmospheric particulate matter in China have mainly been concentrated in the Beijing-Tianjin-Hebei urban agglomeration, Yangtze River Delta, and Pearl River Delta urban agglomeration, with few studies conducted in northeast China. Zhang et al. (2020) speculated that the main source of aerosol particles that cause heavy haze pollution in northeast China is the accumulation of primary organic matter emitted from residential coal burning, with further deteriorations in air quality due to secondary aerosol formation via heterogeneous reactions. The second most important source was reported to be the long-range transport of agricultural biomass burning emissions. Hong et al. (2019) found that the growth rate of atmospheric NO_3^- concentrations exceeds that of SO_4^{2-} during heavy haze weather, and is an important phenomenon during winter haze pollution in northeast China. The rapid generation of SO_4^{2-} during haze is closely related to the aqueous reaction under high water vapor pressure. Nitrate homogeneous gas-phase reactions are an important feature of NO_3^- generation during haze pollution. Coal is the main fuel in northeast China. Unlike other areas of China, most of the local coal has a low-sulfur content. In addition, northeast China is the northernmost part of the country, and the winter is long and severely cold. The specific emissions and meteorological conditions of the region will have an impact on secondary particulate matter formation. In addition, monitoring stations are mainly located in big cities, with few observations in small cities, suburbs, and rural areas. It is therefore difficult to fully understand the mechanism of regional haze formation from the distribution of pollution sources, atmospheric physics, and chemical processes. Therefore, this study established 14 sampling sites in three different cities, and their suburbs and surrounding rural areas in northeast China to simultaneously observe the atmospheric PM_{10} and $\text{PM}_{2.5}$ mass concentrations, their chemical components, and the precursor gas concentrations. The characteristics and production mechanisms of secondary particulate matter (i.e., SO_4^{2-} and NO_3^-) under low-sulfur emission and low-T conditions has led to differences in the haze pollution process compared to other regions of China. The changes in secondary particulate matter concentrations due to meteorological factors and precursor gases, and the differences with other regions of China were investigated. The important role of the increase in the secondary particulate matter concentration during the formation of regional persistent haze pollution was also examined.

Sampling And Analysis

2.1 Sampling and analysis

A total of 14 sampling sites were set up in urban, suburban, and rural locations in northeast China. Simultaneous observations of PM_{10} and $\text{PM}_{2.5}$ mass concentrations in winter were conducted from 2017 to 2019, and the chemical components of $\text{PM}_{2.5}$ were analyzed during the four most polluted periods. The detailed locations of each site are shown in Figure 1. The four episodes were: EP1 from December 26, 2017 to January 9, 2018 (15 days); EP2 from December 10–17, 2018 (eight days); EP3 from January 10–15, 2019 (six days); and EP4 from February 13–4, 2019 (20 days). The four episodes lasted for a total of 49 days. The letters in the figure represent the 14 sampling sites. The urban sampling sites were Hashengtai Station in Harbin (HST); Beihai Station in Changchun (BH); Qianguo Station (QG), Daqing Station (DQ), Shenyang Station (SY), and Siju Station (SJ) in Harbin, DLS Station in Changchun (DLS), and Beilin Station (BL) and Yongji Station (YJ) in Jilin. The rural sites were BinXian Station (BX), Zhaodong Station (ZD), Yushu Station (YS), Siping Station (SP), and Gangzicun Station (GZC).

A Dandong Smart Medium Flow Sampler was used for $\text{PM}_{2.5}$ sampling, with a flow rate of 28.3 L min^{-1} . Whatman's quartz film was used to collect particle samples (Whatman, UK). The sampling frequency was once a day for 24 h. The filter membrane was wrapped with tin foil before sampling and roasted in a muffle furnace at 550°C for 5 h to remove the residual organic matter and impurities. Before and after sampling, the quartz membrane was placed in a constant T and RH box (50% RH, 25°C) for 48 h, weighed with a 100,000 balance (accurate to 0.01 mg), and the mass of the collected particulate matter was determined by subtraction. Using the flow rate and duration of sampling, the $\text{PM}_{2.5}$ mass concentration was calculated. The sample was stored in tin foil in a refrigerator (-20°C) until analysis.

The chemical analysis included water-soluble ions (F^- , Cl^- , NO_3^- , SO_4^{2-} , NH_4^+ , Na^+ , K^+ , Ca^{2+} , and Mg^{2+}) and OC and elemental carbon (EC). The detection limit of each ion was less than 0.003 mg L^{-1} . For the analysis, 1/4 of the filter membrane was placed in 20 ml ultrapure water (Millipore, USA, $18.2\text{ M}\Omega$) and treated three times in an ultrasonic bath. The extract was measured with ion chromatography (ICS2500 and ICS2000, Dionex, USA). The OC and EC

analysis was conducted with a thermal/optical carbon analyzer (Sunset Laboratory Inc., USA). The CLEANOVEN program was run prior to the analysis to remove possible interferences in the instrument. To detect the amount of particulate organic carbon (POC) generated, the sample was irradiated with a 633 nm laser to measure the change in reflected light intensity during heating. The return of the reflection intensity was defined as the start point of the EC, and POC was isolated from EC1 to accurately determine the separation of OC and EC. Ultimately, the total OC of the particulate samples was defined as $OC = OC1 + OC2 + OC3 + OC4 + POC$, and EC was defined as $EC = EC1 + EC2 + EC3 - POC$.

The PM_{10} , $PM_{2.5}$, SO_2 , NO_2 , O_3 , and CO data was collected from the Liaoning real-time air quality publishing system (<http://211.137.19.74:8089/Home/RealTime>). Meteorological data was obtained from the China Meteorological Administration Intranet CIMSS Data (http://10.86.121.55/cimissapiweb/apiwebuserinfo_toPersonalSpa.action).

2.2 Quality control and quality assurance

Quality control was performed in strict accordance with the relevant technical specifications. Blank samples were analyzed, and each analytical instrument was calibrated with standard materials. The correlation coefficient of the water-soluble ion calibration curve was not less than 0.995, and the standard recovery rate was between 80% and 120%. The OC/EC ratio was manually calibrated at the beginning and end of the daily analysis. The deviation in the corrected peak area was within 3.0%, and was quantitatively calibrated with a 5% CH_4/He internal standard to ensure that it was within the quality control range. The correlation between manual sampling and online air monitoring results was significant ($P < 0.05$), and 14 instruments were compared in parallel before sampling to ensure that the results were accurate and comparable.

Results And Discussion

3.1. Temporal changes of the pollution characteristics in four haze pollution episodes in northeast China during 2017–2019

Table 1 and Figure 2 show the $PM_{2.5}$ concentration ($\mu g m^{-3}$) and the concentrations of its chemical components during the sampling period at each sampling site. In EP3, only four sampling sites were analyzed, and they were not included in the calculation of total $PM_{2.5}$. The $PM_{2.5}$ concentration was 66.3–158.5 $\mu g m^{-3}$, with an average of 104.7 $\mu g m^{-3}$. This was 1.4 times China's national environmental standard (24 h average of 75 $\mu g m^{-3}$) and 4.2 times the World Health Organization (WHO) standard ($\sim 25 \mu g m^{-3}$). The highest concentration was observed at HST, with the stations following the order of $HST > BX > SP > SJ > YS > ZD > DLS > SY > GZC > BH > BL > DQ > SY > YJ$. The $PM_{2.5}$ concentrations were 158.5, 144.1, 129.8, 124.5, 122.9, 111.3, 95.8, 93.9, 91.5, 90.8, 84.7, 77.3, 74.3, and 66.3 $\mu g m^{-3}$.

The chemical component concentrations at each sampling site were in the range of 52.4–109 $\mu g m^{-3}$, accounting for 63.8–82.1% of the $PM_{2.5}$, with an average of 72% (Table 2). Total carbon (TC) was the component with the highest concentration (31.2 $\mu g m^{-3}$), accounting for 29.8% of the $PM_{2.5}$. This was followed by water-soluble ions, with a concentration of 29.3 $\mu g m^{-3}$, accounting for 28% of the $PM_{2.5}$. The winter heating period in northeast China has a duration of five months, and the large amounts of coal-fired emissions resulted in the contribution of organic matter to PM being much higher than in other seasons (~ 30 –40%, Sun et al., 2013). Organic carbon (OC) was the most important component of $PM_{2.5}$, with a concentration of 26.3 $\mu g m^{-3}$, followed by NO_3^- and SO_4^{2-} , with concentrations of 8.3 and 7.0 $\mu g m^{-3}$, respectively. Total carbon, NO_3^- , SO_4^{2-} , and NH_4^+ accounted for 29.8%, 7.9%, 6.7%, and 5.3%, respectively, and in Beijing-Tianjin-Hebei accounted for 28%, 19%, 12%, and 11%, respectively, in the same time period (Wang, 2021a). The proportion of TC in $PM_{2.5}$ in northeast China was higher than in the Beijing-Tianjin-Hebei region, but the other components had a lower proportional content. The absolute concentration and proportional content of NO_3^- in northeast China has surpassed that of SO_4^{2-} , and it has therefore become the most important secondary inorganic component of $PM_{2.5}$. The rapid increase in the NO_3^- concentration during the pollution period has become one of the key factors in the explosive growth of $PM_{2.5}$. The reason for this is the use of low-sulfur coal in the northeast. Low-sulfur coal reduces sulfur emissions and greatly reduces the overall concentration and proportional content of SO_4^{2-} in $PM_{2.5}$. In the winter the low T reduces the pH of $PM_{2.5}$, which is conducive to NO_3^- production (Shi et al., 2019). The chemical component concentrations followed the order of $NH_4^+ > EC > Cl^- > K^+ > Na^+ > Ca^{2+} > Mg^{2+} > F^-$, with concentrations of 5.5, 4.9, 4.2, 1.7, 1.5, 0.8, 0.2, and 0.1 $\mu g m^{-3}$ respectively. SO_4^{2-} , NO_3^- , and NH_4^+ (SNA) accounted for 19.9% of $PM_{2.5}$ and 71% of total water-soluble ions. Organic matter and SNA were the main components of $PM_{2.5}$. The main chemical components that contributed to haze pollution in northeast China were organic matter and inorganic water-soluble ions. These components were mainly derived from photochemical oxidation and the liquid-phase oxidation reactions of gaseous precursors.

Table 1
Average concentrations (μgm^{-3}) and the proportional content (%) of the chemical components of $\text{PM}_{2.5}$

	$\text{PM}_{2.5}$	F^-	Cl^-	NO_3^-	SO_4^{2-}	Na^+	NH_4^+	K^+	Mg^{2+}	Ca^{2+}	OC	EC	TWSIs*	TWSIs/ $\text{PM}_{2.5}$	TC	TC/ $\text{PM}_{2.5}$
HST	158.5	0.4	6.7	9	9.6	1.5	7.3	2.3	0.1	0.4	50.1	8.4	37.2	23.5	58.5	36.9
SJ	124.5	0.1	4.7	9.5	7.7	1.6	6.5	2.2	0.1	0.5	34.3	6	32.9	26.4	40.3	32.4
BX	144.1	0.2	4.8	10.8	8.1	1.4	6.5	2.8	0.2	0.5	30.4	6.3	35.2	24.4	36.7	25.5
ZD	111.3	0.1	4.4	6.2	7.1	1.4	4.6	2	0.1	0.9	28.5	4	26.8	24.1	32.5	29.2
BL	84.7	0.1	1.7	4.1	4.5	1.7	2.8	1.2	0.1	0.4	28	7.9	16.6	19.6	35.9	42.4
DQ	77.3	0.1	2.5	6.3	5.4	2.3	3.4	1	0.1	1.3	16.4	2.8	22.4	29	19.2	24.8
YJ	66.3	0.1	2.6	5.3	5.8	2	3.7	1.5	0.1	1	15.6	2.5	22.1	33.3	18.1	27.3
BH	90.8	0.1	4.1	9.4	6.5	1.3	5.9	1.5	0.1	0.6	20.9	3.4	29.5	32.4	24.3	26.7
GZC	91.5	0.1	4.4	11.2	7.5	1.6	6.6	1.8	0.1	0.9	20.8	3.8	34.1	37.3	24.7	26.9
DLS	95.8	0.1	5	9.3	7	1.2	4.8	1.1	0.8	1.8	21.4	6.2	31.1	32.4	27.6	28.9
SY	74.3	0	3	4.2	4.5	0.9	3.2	1	0.1	0.4	16.8	4.2	17.3	23.3	21	28.3
YS	122.9	0.1	5	8	6.2	1	6.1	1.7	0.1	1.2	31.7	5.3	29.5	24	36.9	30.1
SP	129.8	0.1	6.4	11	7.7	1	7.2	2.4	0.1	0.2	35.4	4.8	36.1	27.8	40.2	31
SY	93.9	0.1	4	12.5	9.7	1.8	8.3	1.3	0.3	1.1	18.6	2.9	39.1	41.6	21.5	22.9
average	104.7	0.1	4.2	8.3	7	1.5	5.5	1.7	0.2	0.8	26.3	4.9	29.3	28	31.2	29.8
average/ $\text{PM}_{2.5}$	100	0.1	4.0	7.9	6.7	1.4	5.3	1.6	0.2	0.8	25.1	4.7	28.0	/	29.8	/

The common feature of the $\text{PM}_{2.5}$ chemical component analysis was that the Harbin-centered area was more polluted than Changchun (Table 1, Figure 3). Harbin and its nearby areas had the highest OC and EC levels, the SO_4^{2-} and NO_3^- concentrations were highest in Shenyang, and the K^+ concentration was higher in rural areas than in urban and suburban areas.

Table 2
The concentrations of $\text{PM}_{2.5}$ and its chemical components in three pollution episodes (μgm^{-3})

	$\text{PM}_{2.5}$	F^-	Cl^-	NO_3^-	SO_4^{2-}	Na^+	NH_4^+	K^+	Mg^{2+}	Ca^{2+}	OC	EC
EP1	86.1	0.1	4.3	6.5	7.2	1.6	4.6	1.4	0.1	0.6	23.6	2.6
EP2	86.9	0.1	2.4	5.6	4.1	1.4	5.2	1.5	0.1	0.7	20.4	4.8
EP4	122.4	0.1	5.2	10.8	7.3	0.5	5.3	1.8	0.2	0.4	27.4	5.6
total	98.5	0.1	3.9	7.6	6.2	1.2	5	1.5	0.1	0.6	23.8	4.3

Comparing the three pollution episodes shown in Table 2, EP4 (in 2019) had the highest concentrations of $\text{PM}_{2.5}$ and its chemical components, while there was little difference between EP2(in 2018) and EP1(in 2017).

3.2 The evolution of $\text{PM}_{2.5}$ and its chemical composition and the causes of pollution during the fourth pollution episode

Figure 4 shows the temporal changes of PM_{10} and $\text{PM}_{2.5}$, their chemical components and precursor emission gas concentrations, meteorological factors, and the height of the boundary layer during the four pollution episodes. The evolution of EP1–EP4 in terms of the $\text{PM}_{2.5}$ concentration and its chemical composition, and the causes of pollution are analyzed below.

EP1 was formed by the combined effect of the accumulation of local coal emissions, secondary conversion under a low T and high RH, and regional transmission. Wind direction and wind speed were the primary meteorological factors that affected the pollutant concentration. The important indicators of the beginning and end of the pollution episodes was the change of wind direction and speed. Pollution started to accumulate on December 26, 2017, and when the wind direction changed to the southwest, $\text{PM}_{2.5}$ concentrations increased in various locations. The $\text{PM}_{2.5}$ concentration peaked on January 1, 2018, when the wind speed was very low (Figures 4a, b; Figure 5). The wind turned to the north on January 1, the

wind speed increased, and the $\text{PM}_{2.5}$ concentration decreased rapidly, with the pollution episode ending on January 9. Whenever the wind direction turned to the south and the wind speed decreased, the $\text{PM}_{2.5}$ concentration gradually accumulated, but when the wind direction was northerly the wind speed increased and the concentration decreased rapidly (Figures 4 and 5). The trends of SO_2 and NO_2 were similar to those of $\text{PM}_{2.5}$, indicating that emissions had a great impact on pollution. The SO_2 and NO_2 levels in EP1 were the highest of the entire three years. The boundary layer height (BLH) followed the opposite pattern to that of the pollution concentration (Figure 4x). A low BLH results in poor diffusion of pollutants and high pollutant concentrations, which plays an important role in the rise and fall of the pollutant concentration (Figure 4v). The effects of air T and RH were also significant, and pollution in EP1 increased as the T increased (Figure 4p). However, the T on January 2–8 was higher than on the most polluted day December 31–January 1. It was apparent that T did not play a decisive role in pollution episodes. When the RH was high, the pollution was heaviest (Figure 4w). A high RH was very important for pollution formation.

The OC/EC ratio is used to characterize carbon aerosol emissions and conversion characteristics. Different ratios represent different sources of pollution. A ratio between 1.0 and 4.2 typically represents exhaust emissions from diesel and gasoline vehicles (Schauer et al., 2002); and a ratio of 2.5–10.5, represents emissions from coal combustion (He et al., 2004); while ratios of 9–12.3 and 16.8–40, represent biomass combustion emissions (Cao et al, 2005; Zhang et al., 2007). The average OC/EC ratio of the four episodes was 6.6 (1.5–25.6) (Figure 4s), indicating that they were all affected by secondary aerosol. Compared with the other three EPs, the OC/EC ratio was highest in EP1. The rural station SP had the highest OC/EC ratio, with a value exceeding 15 on six days. This was mainly due to the burning of rural straw. At the same time, the K^+ , NH_4^+ , and Cl^- concentrations, which were indicative of combustion emissions were also high, which indicates that they not all emissions were from straw combustion (Cao et al., 2010). The OC/EC ratio at HST was between 5–12.5, indicating that the main source of its air pollution was emissions from coal combustion. The OC/EC ratios at the other stations were also largely in this range, indicating emissions from coal combustion.

The SO_4^{2-} , NO_3^- , and NH_4^+ concentrations in EP1 were very high (6.5, 7.2, and $4.6\mu\text{g}\cdot\text{m}^{-3}$, respectively, Table 2), with only the concentrations in EP4 being higher. The SO_4^{2-} and SO_2 concentrations, which were representative of coal burning, were higher than those of NO_3^- and NO_2 , indicating that the emissions from coal combustion were the most important factor in EP1 (Figures 4p,q, and r). The ratio of secondary pollutants (SNA) to EC is used to evaluate the degree of secondary conversion. The higher the value, the more serious the secondary pollution (Figure 4, Yang et al., 2018; Lin et al., 2009). Elemental carbon is usually considered to be a tracer of a pollution source. Comparing the ratio with the primary emissions (Ca^{2+} , Mg^{2+}) and other components, if the primary emissions are high but the ratio is not high, the pollution is caused by the primary emissions, otherwise it is caused by secondary conversion or regional transmission. The $\text{SO}_4^{2-}/\text{EC}$ and NO_3^-/EC ratios were lowest in EP3 among the four episodes, of which Shenyang and Siping had the highest values (>5). The Ca^{2+} and Mg^{2+} concentrations were not high, and therefore there were obvious regional transmission characteristics. At the other sampling sites, the $\text{SO}_4^{2-}/\text{EC}$ and NO_3^-/EC ratios were very high, indicating that SO_4^{2-} and NO_3^- were formed by secondary conversion. During the secondary conversion process, the T was low and RH was high. The SNA and OC concentrations increased and decreased with the rise and fall of RH (Figure 4). Ge et al. (2012) found that fog promoted the generation of secondary aerosols (SNA and oxidizing organic matter) in the atmosphere. A high RH is conducive to the absorption of the main chemical components in the moisture on the surface of $\text{PM}_{2.5}$, and the pollutant concentration will then increase rapidly (see section 3.3 for details). Therefore, it was concluded that EP1 was a composite pollution process formed by local emissions from coal combustion, secondary conversion under a low T and high RH, and regional transmission.

EP2 was expected to be dominated by straw burning pollutants due to the large-scale straw burning that occurred during the sampling process. The chemical component with the highest concentration was OC (Figure 4g), with a peak concentration of $180\mu\text{g}\cdot\text{m}^{-3}$ at HST. The concentrations at the surrounding BL, BX, and SJ sites were also very high, indicating that straw burning made a significant contribution to OC. The most representative ion for straw burning is K^+ and its concentration was very high, with only EP4 having a higher concentration (Figure 4m). The K^+ concentrations at HST, SJ, SP, BX, BL, and ZD were 5–7 times higher than the typical atmospheric concentration in the main straw burning area. The different sampling sites that were affected by straw burning displayed different characteristics. At HST and BX, OC and K^+ increased significantly at the same time, while the K^+ concentration at SP increased more significantly than the OC concentration. There was a significant increase in OC at BL, whereas K^+ did not increase significantly. These results may be related to the different local emission sources, with HST receiving a large contribution from straw combustion and motor vehicle emissions, SP being impacted by straw combustion, and BL being impacted by residential coal burning in the suburbs.

EP3 was a cross-regional transmission process. Figure 6a clearly shows the gradual reduction of $\text{PM}_{2.5}$ and other pollutants as they were transported from southwest to northeast. The jump point of the $\text{PM}_{2.5}$ concentration changed from SY→BH→SJ→HST (Figure 6b), which indicated that EP3 was clearly dominated by a secondary transmission process. The $\text{SO}_4^{2-}/\text{EC}$ and NO_3^-/EC ratios were the highest among the four pollution episodes, and the peak values of the four sampling sites were in the range of 6.7–18.9 (Figure 4p, q). This further confirms that the event was a regional transfer process.

EP4 was the pollution episode with the highest $\text{PM}_{2.5}$ concentration and the heaviest pollution during the entire observation period. Its main features were a high $\text{PM}_{2.5}$ and O_3 concentration, and a high mid-winter T. The SO_2 and NO_2 concentrations were lower than those of EP1 and EP3. The period was characterized by low emissions, and therefore the high levels of pollution were mainly a consequence of the strong oxidation conditions and high winter T.

There were three pollution peaks in EP4 (Figure 4), with high concentrations of the main chemical components (OC and SNA). The first peak was on February 15. The PM_{10} concentration was highest at BX and YS, which were the representative rural sampling sites, and it was much higher than the $PM_{2.5}$ concentration (Figure 4), indicating that there was a large proportion of coarse particles. However, the NO_3^-/EC and SO_4^{2-}/EC ratios were not very high, indicating that primary pollutants were the major contributors to the pollutant load. The BX site had the highest SO_4^{2-} and CO concentrations, as well as high concentrations of NO_2 , OC, EC, Cl^- , NO_3^- , NH_4^+ , and K^+ and other coal-burning emission index ions (Wang et al., 2021a; Hu et al., 2015). The YS site also had high concentrations of chemical components. These sites were located in rural areas, with few motor vehicles, and the high concentrations were likely caused by high emissions of loose coal and biomass combustion.

The second peak occurred on February 21. The wind direction at each station was southerly. The $PM_{2.5}$ concentration at BX, HST, and SJ was high (Figure 4b), the weather conditions were stable, and the wind speed was low to calm (i.e., less than 2m/s) (Figure 5). The T continued to increase and the RH was conducive (about 50%) to the conversion to secondary pollutants. The high concentration at HST was related to the high SO_2 , NO_2 , and CO emissions on the previous day. On February 20th in BX, the NO_3^- and SO_4^{2-} concentrations were high, the OC concentration at SJ was high, and the EC concentration at BX and SJ was high. These results indicated the secondary generation of local coal emissions under suitable T and RH conditions in a small area. The pollution process occurred under the joint action of atmospheric diffusion (see section 3.3 for details).

The $PM_{2.5}$ concentration in the third peak was the highest during the entire observation period. There were three main reasons for this.

■ The photochemical generation of high levels of secondary organic carbon (SOC). The high levels of SOC (Figure 4t, estimated by the OC/EC minimum ratio method, $SOC = OC - EC \times (OC/EC)_{min}$. Li et al., 2018a) accounted for the highest proportion of OC (Figure 4u). The O_3 concentration and T were also the highest during the entire observation period (Figure 4e and v). The high O_3 concentration enhances the atmospheric oxidability, which coupled with the high T, was conducive to SOC formation. Li (2018a) and Hu et al. (2012) in Zibo and the Pearl River Delta both found that SOC and O_3 increased in a similar manner.

■ A large amount of secondary generation of SNA. The SNA concentration was only higher in EP3 due to regional transmission. However, the SO_2 concentration was the lowest among the four pollution episodes, and the NO_2 concentration was the same as in EP1. Due to the low emission levels, the high pollution load was created by high secondary pollutant concentrations. There were two main reasons for this. First, under a relatively high T (0–5°C) and RH (40–60%), which was not high enough to limit the reaction, the gas emitted by local coal and motor vehicles generated a high SNA concentration through homogeneous and heterogeneous phase reactions (see section 3.3 for details).

Similarly, SJ, HST, DQ, ZD, and SY had high $PM_{2.5}$ concentrations, which may be related to their higher local emissions. The OC, EC, and Cl^- concentrations at SJ and ZD were high on February 26–28, the OC and EC concentrations at DQ and HST were high on February 28, and the SNA concentration at SY had been continuously increasing since February 27. This indicates that the peaks were mainly the local secondary conversion of primary emissions. At this time, the SO_4^{2-} concentration was high (Figure 4k, peak value 6.1–20.4 $\mu g m^{-3}$), but still lower than the NO_3^- concentration. The NO_3^-/SO_4^{2-} ratio was mostly >1, with the highest value reaching 2.5 (Figure 4r).

The reason why the NO_3^- concentration was higher than the SO_4^{2-} concentration was related to the low SO_2 emission concentration, which limited SO_4^{2-} formation. It may also be related to the high O_3 concentration and the strong gas oxidation was conducive to the gas-particle conversion of NO_3^- . The high O_3 concentration had an important effect on NO_3^- and SO_4^{2-} formation. Studies have found that under suitable light conditions, the photolysis of O_3 will produce OH $\cdot$ and promote NO_3^- and SO_4^{2-} formation (An et al. 2014) (see section 3.3.1 for details). Wang et al. (2018) found that the low T of urban high-rise buildings and the high O_3 concentration in the residual layer at night can promote the gas-particle conversion of NO_3^- and the heterogeneous reaction of N_2O_5 . In this study, NO_3^- formation was dependent on the combination of a high T in winter and a high O_3 concentration. This involved the formation of low-T gas-particles at night, and the formation of high-T photochemical reactions during the day. It can be seen that the increase in the O_3 concentration greatly increased the NO_3^- and SO_4^{2-} concentration, and it is therefore very important to strengthen the control of O_3 and NO_x pollution.

■ The superimposed effect of cross-regional transmission has caused the rapid growth of secondary pollutants. The SO_4^{2-}/EC and NO_3^-/EC ratios in Figure 4q and r are very high, indicating that secondary formation occurs through the superimposition of regional transport and secondary reactions. The OC/EC ratio was not high (Figure 4s, between 1.7 and 8.4, with an average of 4.9), indicating that it was mainly controlled by emissions from coal combustion and motor vehicle exhaust emissions. It can be seen from the graphs of the $PM_{2.5}$ concentration and wind field in Figure 7 that the most polluted area was near Harbin (HST). At this time, the wind direction and wind speed of each station changed from northerly to southerly, and the wind speed decreased rapidly. This shows that the atmosphere was in a static and stable state, and the static and stable meteorological conditions were also conducive to the accumulation of secondary particulate matter. In addition, the wind field at the high-concentration center of the BL site had an obvious counterclockwise convergence, and the wind speed was higher than that in the surrounding areas, which accelerated the accumulation of pollutants at the site.

It can be seen that EP4 was a compound pollution process. The Cl^- and OC concentrations were the highest among the four episodes, indicating that coal combustion made a substantial contribution, and the K^+ and Mg^{2+} concentrations were also the highest among the four episodes. Biomass combustion and industrial emissions also made a large contribution. Except for the high Ca^{2+} concentration at the BX and ZD sites on February 21st, the levels at the other stations were low. The main source of Ca^{2+} is usually sand and dust emissions (Xu et al., 2017b), indicating that the impact of sand and dust was small in EP4. Therefore, the pollution formation during this episode occurred through the homogeneous and heterogeneous reaction of pollutants emitted by local coal combustion, biomass combustion (K^+), and industrial emissions (Mg^{2+}) under a moderate T and strong gas oxidizing conditions (high O_3). It was formed by a significant increase in the secondary pollutant concentrations, such as SOC and SNA, and then superimposed on a composite pollution process controlled by regional transmission.

3.3 The influence of meteorological factors (e.g., T and RH) on secondary pollutant (SO_4^{2-} and NO_3^-) formation in the haze pollution process

3.3.1 Nitrate formation

The rapid increase in secondary pollutant (SO_4^{2-} and NO_3^-) concentrations is an important reason for haze formation, and meteorological factors also play an important role in secondary pollutant formation.

Nitrate formation in the northeastern urban agglomeration was investigated. The relationship between $[\text{NH}_4^+]_{\text{excess}}$ and $\text{NH}_4^+ / \text{SO}_4^{2-}$ (molar concentration ratio; Pathak et al., 2009) was used to determine the occurrence of NO_3^- under different pollution processes and different weather conditions, and homogeneous and heterogeneous chemical reactions. The $[\text{NH}_4^+]_{\text{excess}} = ((\text{NH}_4^+ / \text{SO}_4^{2-} - 1.5) \times [\text{SO}_4^{2-}])$ was calculated during the entire observation period. Figure 8 shows its correlation with NO_3^- . During the pollution process, NO_3^- and $[\text{NH}_4^+]_{\text{excess}}$ had a strong linear relationship ($R^2=0.81$), indicating that NO_3^- was mainly generated through heterogeneous reactions (Pathak et al., 2005). The NO_3^- concentration increased with the increase in $[\text{NH}_4^+]_{\text{excess}}$ (Figure 8a). Therefore, the NO_3^- formation in the northeastern urban agglomeration occurred mainly through the homogeneous gas-phase reaction of atmospheric ammonia (NH_3) and nitric acid (HNO_3).

The NO_3^- formation conditions and accumulation mechanisms differ under the influence of different emission and meteorological factors. In recent years, the NO_x concentration was often higher than that of SO_2 . The low slope value of Figure 8a (0.62) indicates that the NH_4^+ concentration in northeast China was much higher than that of NO_3^- , which was conducive to NO_3^- formation. Because emissions from coal combustion make a large contribution to atmospheric NH_4^+ and Cl^- (Xu et al., 2017b), the Cl^- concentration was added to evaluate the relationship between $[\text{NH}_4^+]_{\text{excess}}$ and NO_3^- (Figure 8b). The correlation coefficients for the relationships between $[\text{NH}_4^+]_{\text{excess}}$ and $\text{NO}_3^- + \text{Cl}^-$ in all pollution processes were greater than 0.82, and for EP4 the value was 0.99. The slope was also very high, indicating that after NH_4^+ neutralized all of the NO_3^- and SO_4^{2-} (forming ammonium nitrate (NH_4NO_3) and ammonium sulfate ($(\text{NH}_4)_2\text{SO}_4$)), there may be a surplus, which would continue to react with Cl^- and other anions, mainly in the form of ammonium chloride (NH_4Cl). In EP1 and EP4, the slopes were 1.1 and 1.14, and the intercepts were 0.09 and 0.12, respectively, indicating that some of the $\text{NO}_3^- + \text{Cl}^-$ was not completely neutralized by NH_4^+ . In Figure 4n, it can be seen that the Ca^{2+} concentration in EP1 was higher than in the other pollution episodes, and the contribution of sand dust was also greater. The remaining NO_3^- and Cl^- may exist in the form of calcium nitrate ($\text{Ca}(\text{NO}_3)_2$) and calcium chloride (CaCl_2). The lowest slope of EP2 was 0.68, indicating that after all the $\text{NO}_3^- + \text{Cl}^-$ was neutralized, there was still a large amount of NH_4^+ . The main feature of EP2 was that straw burning produced a large amount of NH_3 , and therefore the NH_4^+ concentration was also high. The slope of EP3 was 1.04, indicating that NH_4^+ was present in excess and Cl^- emissions from coal combustion were not high. The K^+ concentration in EP4 was high. The contribution of biomass combustion was also high, which may have enabled potassium to exist in the form of potassium nitrate (KNO_3) and potassium chloride (KCl).

Nitrate in the EP1 process was formed under the conditions of a medium T and high RH. At this time, the warming period in winter was occurring (Figure 8d, 5v), and the RH was also high when NO_3^- peaked (Figure 8c, 5w). This shows that NO_3^- formation occurred when the T was mild in winter and the RH was high. A high T was conducive to the homogeneous gas-phase reaction of NO_2 reacting with $\text{OH}^\bullet$ to produce gaseous HNO_3 (Harris et al., 2013). A T not higher than 4°C is also conducive to NO_3^- formation. The reaction therefore proceeded in the positive direction (Sun et al., 2012). The subsequent reaction between gaseous HNO_3 and NH_3 needs to occur at a higher RH, because although NO_3^- is mainly formed through a homogeneous reaction in the gas-phase, a high RH is conducive to the accumulation of NO_3^- in the particles (Shi et al., 2014). Therefore, a high RH promotes NO_3^- formation.

The EP2 process was clearly impacted by straw burning emissions, with rapid NO_3^- formation in an NH_3 -rich environment. Straw burning in the vicinity of several cities, coupled with southerly winds, was conducive to the spread of pollution from south to north. In particular, the wind speeds at several sampling sites were high on December 15 (Figure 5, $4\text{--}5\text{ms}^{-1}$), which caused pollution to rapidly spread to the area. On the December 16 the wind speed decreased rapidly, and the calm winds were conducive to the accumulation of pollutants. At this time, at SP, YS, and other locations, the RH was high (40–60%, Figures 4w and 8c), and the T was low (-15 to -11°C , Figure 4v), and therefore straw burning pollutants accumulate in wet weather conditions to produce haze. There are records of haze in various locations.

In the EP3 pollution process, the NO_3^- concentration was the highest among the four pollution episodes (Figure 4j, Figure 9a). It was formed by the secondary pollutants in the high RH and medium T environment during the transmission process, and the RH has a great influence on it. The RH was also the highest of the four periods at around 50–80% (Figures 9a, c and Figure 4w), and the T was centered at $-10-0^\circ\text{C}$ (Figure 4v).

The NO_3^- formation in the EP4 process occurred under a relatively high T and moderate RH in winter. Only EP3 had a higher NO_3^- concentration, with the NO_3^- concentration in the third peak period being especially high (Figures 4j, 9a). The RH was only between 40–60% (Figures 4w, and 8a, c). Although the RH was not high, the deliquescent RH of the particulate matter was still higher than the weathered RH, which caused it to continue to deliquesce without being weathered, and a high water content was maintained in the particulate matter. In conjunction with the high winter T and strong atmospheric oxidability, serious haze pollution could still occur. The pollution concentration sometimes exceeded the concentration recorded when the RH was higher and the T was lower (such as in EP1). It can be seen that the influence of RH on NO_3^- in northeast China was not as obvious as its influence on SO_4^{2-} . Li et al. (2017), Sun et al. (2013), and Wang et al. (2014) also reached similar conclusions in a study of pollution in the Beijing-Tianjin-Hebei region. Wang et al. (2014) estimated that the influence of fog was responsible of 70% of the SO_4^{2-} formation in winter in Beijing, while the impact on NO_3^- was less than 30%. Under the condition where a certain RH was maintained, a higher T was more conducive to the homogeneous reactions involved in NO_3^- formation.

In the EP4 process T conditions were very favorable, with the highest Ts recorded during all observations (between -4 and -2°C , Figure 8a, d). A higher T is more conducive to the occurrence of photochemical reactions. In addition to the above-mentioned low RH conditions that did not affect NO_3^- formation and the warmer T conditions in winter, the oxidative properties of the atmosphere were also important for HNO_3 formation. During EP4, there were high O_3 concentrations (Figure 4e), and nitrous acid (HONO) peaks also appeared at the same time as the first two peaks of NO_3^- (Figure 9b). The SO_4^{2-} , NO_3^- , HONO, HNO_3 , and NH_3 concentrations in Figure 10 were measured by the Marga instrument in the Shenyang Atmospheric Composition Station. At this time, NO_3^- and SO_4^{2-} formation occurred through the gas-phase oxidation reactions of $\text{OH}\cdot$ with NO_2 and SO_2 , respectively (Seinfeld and Pandis, 2006). The main sources of $\text{OH}\cdot$ were the photolysis of O_3 and HONO (Ji et al., 2016). Although the scattering, reflection, and refraction of haze pollution in winter will weaken the amount of solar radiation reaching the ground and affect the generation of $\text{OH}\cdot$, high HONO concentrations can produce large amounts of $\text{OH}\cdot$ under suitable light conditions, ensuring the uniform progress of the homogenous NO_3^- formation reaction. During the daytime, HONO photolysis produces $\text{OH}\cdot$, $\text{OH}\cdot$ reacts with VOC and NO_x in a multi-chain reaction, and this increases the O_3 concentration. The O_3 further promotes $\text{OH}\cdot$ production through photolysis, and $\text{OH}\cdot$ continues to oxidize NO_2 and SO_2 , which promotes HNO_3 and SO_4^{2-} formation (An et al. 2014). The reaction rate is related to the amount of liquid water adsorbed on the particle-air interface. Strong correlations have been reported between aerosol and HONO concentrations, and the specific surface area of an aerosol and the HONO concentration (Finlayson-Pitts et al., 2003). Part of the reaction product is separated from HONO when the reaction surface returns to the atmosphere, while HNO_3 stays on the reaction surface and re-participates in a series of atmospheric chemical reactions, increasing the NO_3^- concentration in the atmosphere. Therefore, the high atmospheric oxidability formed by the high O_3 and HONO concentrations in the EP4 process promoted photochemical reactions and produced a large amount of NO_3^- .

Similarly, during EP4, a high NH_3 concentration was observed, which reacted with HNO_3 (Figure 9b) and promoted massive NO_3^- aerosol formation. Due to the use of low-sulfur coal and the widespread use of desulfurized rubber as pollution control measures, SO_2 concentrations have decreased, but NH_3 emissions have risen at the same time. The NO_3^- concentration increased significantly with the increased NH_3 emissions (Figure 9a). The relatively warm T (-4 to -2°C) was conducive to an acceleration of the neutralization reaction of NH_3 and HNO_3 , which promoted NO_3^- formation. Many studies have also shown that a sufficient source of NH_3 will effectively promote NO_3^- and SO_4^{2-} particulate formation, resulting in the rapid accumulation of particulate matter (2015; Guo et al., 2017). A high NH_3 concentration promotes NO_3^- aerosol formation in a ubiquitous atmospheric chemical phenomenon that has also been observed in other cities in northern China (Sun et al., 2018). In addition, under a high RH and rich NH_3 conditions, SO_4^{2-} will also be generated in large quantities. The pH of the aerosol surface is close to 7, and NO_2 oxidizes SO_2 to generate SO_4^{2-} (Wang et al., 2016a). However, Li et al. (2018b) later found that on the surface of aqueous sodium bisulfite (NaHSO_3) (pH 3~6), NO_2 cannot directly oxidize S(IV) to form SO_4^{2-} , but instead generates NO_3^- and HONO. Based on this analysis, the possibility of HONO oxidation of S(IV) is a more important mechanism of NO_3^- formation. In this study, the NO_3^- formation in northeastern China was mainly due to the mild T, high RH, high atmospheric oxidability (O_3 and HONO), suitable light conditions, and a high NH_3 concentration. A homogeneous gas-phase reaction occurred between $\text{OH}\cdot$ and NO_2 , SO_2 , and NH_3 .

3.3.2 The relationship between the SO_4^{2-} concentration and water vapor pressure

To characterize the relationship between ion concentrations and RH, the relationship between ambient water vapor pressure(e^*) and the SO_4^{2-} concentration was determined for different pollution periods, under different RH, T, and sulfur oxidation rate (SOR) conditions, and with different precursor gas concentrations (mainly SO_2 and NO_2). The ambient water vapor pressure was calculated using the formula $e^*=e \times \text{RH}/100$ (e refers to the saturated water vapor pressure, where $e=6.112\exp(17.67t/(t+243.5))$, t refers to the T ($^\circ\text{C}$)). The SOR refers to the molar ratio of sulfur in SO_4^{2-} to the

total sulfur, and is calculated with the formula $SOR = SO_4^{2-} / (SO_4^{2-} + SO_2)$. Figure 10 shows the changes in the SO_4^{2-} concentration with e^* , with air temperature, different pollution periods, RH, and the precursor gases shown in different colors.

The trend of the fitted line in Figure 10a shows that SO_4^{2-} increased with an increase in e^* , but the increase was not very obvious, indicating that SO_4^{2-} formation was complicated. Taking $e^*=1.5$ and the SO_4^{2-} concentration = $10 \mu\text{gm}^{-3}$ as boundaries, the figure could be divided into four areas. Figure 11 shows the statistical values of various pollutants, T, and RH in the four areas.

Area I. This feature mainly occurred in EP4 and EP3 (Figure 10a, b). This area of the figure had the highest SO_4^{2-} concentration ($14.7 \mu\text{gm}^{-3}$), the highest T and O_3 (3.7°C and $71.6 \mu\text{gm}^{-3}$, Figure 10a, Figure 11), coupled with high HONO and NH_3 concentrations (Figure 9b). The degree of oxidation of NO_2 and SO_2 was enhanced, and the SOR (0.3, Figure 10d), SO_4^{2-} ($14.7 \mu\text{gm}^{-3}$), and NO_3^- ($22.3 \mu\text{gm}^{-3}$) increased the most. Although the SO_2 concentration was low, the NO_2 concentration was high, and the prevailing conditions still supported SO_4^{2-} formation. At the same time, the RH was not high (Figure 10d, Figure 11, 63.8%), which affected the aqueous phase reaction of SO_4^{2-} to a certain extent. In area I, the correlation between SOR and O_3 was highest (0.473, Table 3), and the correlation with T (0.275) was higher than the correlation with RH (0.110),

indicating that SO_4^{2-} was mainly transformed by the SO_2 gas-phase instead of aqueous oxidation. Therefore, the SO_4^{2-} formation in area I was mainly the homogeneous gas-phase reaction of the $OH\cdot$ oxidation of NO_2 and SO_2 . The source of $OH\cdot$ was the photolysis of O_3 and HONO, which plays a key role in atmospheric chemistry (Ji et al., 2016). The oxidation rate of $OH\cdot$ is usually several times or even hundreds of times higher than in other pathways (Tang et al., 2006). Many studies have shown that the gas-phase oxidation of SO_2 by $OH\cdot$ and peroxy radicals is important for SO_4^{2-} formation (Xie et al., 2009). Therefore, the photochemical activity had a very important influence on the gas-phase conversion of SO_2 to SO_4^{2-} during the haze events. Previous studies have shown that the heterogeneous chemical reaction of SO_4^{2-} is an important pathway for SO_4^{2-} formation during heavy haze episodes in northern China. The reaction conditions were a low T, high RH, and weak light (Elser et al., 2016), and it was speculated that SO_4^{2-} formation is the gas-phase reaction of $OH\cdot$ oxidation NO_2 and SO_2 . The reaction conditions were warm winter Ts and high O_3 , HONO, and NH_3 concentrations.

The SO_4^{2-} concentration in area II was slightly lower than that of area I, and these conditions mainly occurred in EP1. The conditions that favored SO_4^{2-} formation were the highest SO_2 and NO_2 concentrations, and the highest RH (63.8%). The disadvantages for SO_4^{2-} formation were the very low T (-16°C), weak light levels, low O_3 concentration, and slightly lower SOR (Figure 11). When using the anion/cation equivalent ratio (AE/CE) to evaluate the aerosol acidity (Wang et al., 2016), it was found that the average AE/CE of total cations (NH_4^+ , Na^+ , K^+ , Ca^{2+} , Mg^{2+}) and anions (SO_4^{2-} , NO_3^- , Cl^-) was 1.07 ± 0.21 . After the cations had completely neutralized the anions, there were still small amounts of cations remaining. This indicated that $PM_{2.5}$ was approximately neutral or weakly alkaline. Cheng et al. (2016) also studied the causes of SO_4^{2-} formation under the same conditions (high NO_2 , low O_3 , and high RH) during Beijing haze, and speculated that NO_2 may be an important oxidant for fine aerosols under conditions with high RH and NH_3 neutralization. A high pH value will draw more SO_2 into the aerosol droplets, thereby increasing the rate of SO_4^{2-} formation in the NO_2 reaction pathway. It is more likely that NO_2 will oxidize SO_2 in the aqueous phase on fine aerosols with a high RH (>60–70%) and sufficient neutralization (pH~7) (Wang et al., 2016a). Therefore, it was speculated that the increase in SO_4^{2-} production under high NO_2 and SO_2 concentrations, high RH, and low O_3 levels in northeast China haze events may have a specific mechanism. Under neutral or weakly alkaline conditions, the high pH will pull more SO_2 into the aerosol water, and the high RH will also make it easier for NO_2 to react with SO_2 droplets in an aqueous oxidation to increase the SO_4^{2-} production rate. This is another important reaction pathway for the production of high SO_4^{2-} concentrations in northeast China in addition to the gas-phase transformation under the influence of the photochemical activity in area I. However, due to the unique low-T environment and low SO_2 emissions in northeast China in winter, the aqueous phase reaction of SO_4^{2-} in area II was actually substantially weakened, and the gas-phase SO_4^{2-} formation in area II, with its high atmospheric oxidability, was greater than in area I.

Hong et al. (2019) described seven pollution episodes that occurred in Shenyang from January to April, 2014. The EP1–EP3 reported by Hong et al. (2019) were similar to the EP1 in this study (area II). The emission and meteorological conditions were similar, with high SO_2 and NO_2 concentrations, high RH, low O_3 concentrations, and weak light conditions. EP5 in Hong et al. (2019) was similar to EP4 in this study (area I), both of which had low SO_2 and NO_2 concentrations, low RH, high O_3 , HONO, and NH_3 concentrations, and a high atmospheric oxidability. The SO_4^{2-} formation was also very similar. The pollutant formation pathway in area II might be high-photochemical oxidation or gas-phase oxidation, while area I was an aqueous phase reaction process. Moreover, the SO_4^{2-} concentration produced by gas-phase oxidation was higher than that produced by aqueous phase oxidation. However, gas-phase oxidation often occurred after March in late winter and early spring. Most of the time SO_4^{2-} was produced by an aqueous phase reaction, but the highest concentration and the fastest formation occurred through the gas-phase reaction. Studies in Beijing-Tianjin-Hebei and other regions have shown that the aqueous reaction is the most important reaction pathway for the rapid growth of SO_4^{2-} (Sun et al., 2013). Huang et al. (2015) also reported that the conversion of SO_2 to SO_4^{2-} during winter haze occurred mainly on the surface of aerosol droplets through catalytic oxidation in the presence of transition metals, rather than by gas-phase oxidation. Wang et al. (2016a) studied the heavy pollution formation process

in Beijing-Tianjin-Hebei and the entire North China region in autumn and winter. They also found and confirmed that the aqueous oxidation of NO_2 on atmospheric fine particles is an important SO_4^{2-} formation mechanism during haze episodes in China. The gas-phase oxidation process was not important. However, in northeast China, due to the inhibitory effect of the low T in winter on the SO_4^{2-} aqueous reaction, there is rapid SO_4^{2-} and NO_3^- production, and the rapid gas-phase oxidation process plays an important role. This is the main difference between northeast China and other regions. However, the aqueous reaction is still the most common way of producing SO_4^{2-} in northeast China.

The SO_4^{2-} concentrations in areas Ⅱ and Ⅲ were similar. The largest advantage of area Ⅲ in terms of SO_4^{2-} formation was the high RH, but there were low SO_2 and NO_2 concentrations and a low T, which inhibited the heterogeneous oxidation of NO_2 and SO_2 to a certain extent, resulting in a low SO_4^{2-} concentration. The biggest advantage of area Ⅱ in terms of SO_4^{2-} formation was the high T in winter, but the low SO_2 and NO_2 concentrations and slightly lower O_3 concentration than in area Ⅲ resulted in the degree of homogeneous oxidation of NO_2 and SO_2 in the gas-phase being less than that of area Ⅲ. In addition, the low RH affected the aqueous phase oxidation process causing a low SOR. Therefore, the SO_4^{2-} concentration was not high.

Table 3
The correlation between various pollutants, relative humidity (RH), and temperature (T) in areas Ⅱ and Ⅲ.

	NO_3^-	SO_4^{2-}	T	RH	e^*	SO_2	NO_2	SOR	NOR	O_3
NO_3^-	1	.663**	-.056	.212	.071	.009	.144	.217	.533**	.115
SO_4^{2-}	.822**	1	-.336*	.434**	-.130	.305*	.290	.063	.202	-.054
T	.348**	.110*	1	-.681**	.820**	-.020	-.010	-.248	-.044	-.081
RH	.029	.135**	-.524**	1	-.153	.261	.249	-.056	-.038	.011
e^*	.463**	.231**	.828**	-.009	1	.163	.169	-.354*	-.088	-.116
SO_2	.123**	.338**	-.207**	.184**	-.115**	1	.817**	-.793**	-.585**	-.657**
NO_2	.344**	.426**	.050	.089*	.122**	.687**	1	-.780**	-.696**	-.657**
SOR	.490**	.428**	.275**	-.110*	.268**	-.519**	-.316**	1	.820**	.642**
NOR	.752**	.566**	.354**	-.064	.400**	-.198**	-.169**	.773**	1	.576**
O_3	.216**	.044	.628**	-.412**	.505**	-.459**	-.288**	.473**	.390**	1

Note: **. The correlation was significant at the 0.01 level. *. The correlation was significant at the 0.05 level. The lower left side of the table represents area Ⅱ, and the upper right side represents area Ⅲ.

3.3.3 The influence of T and RH on the concentration of important chemical components

(1) Changes with T:

The NO_3^- concentration increased with increasing T (Figure 12). Higher Ts are conducive to NO_3^- formation in the gas-phase, but Ts below 4°C will not support volatilization and therefore will affect the gas particle distribution in the $\text{NH}_3 + \text{HNO}_3 \leftrightarrow \text{NH}_4\text{NO}_3$ reaction. The formation of SO_4^{2-} was similar to that OC and followed a V-shaped pattern. Higher Ts in winter were beneficial to SO_4^{2-} formation because with high Ts the solar radiation is strong, the rate of photochemical oxidation is rapid, and the OH· concentration increases, which in turn strengthens the oxidation of SO_2 . Under a high RH, the water content of aerosols is relatively high, and O_3 is dissolved in aerosol water where it reacts with dissolved SO_2 to promote the liquid-phase oxidation process (Cheng et al., 2016). Heating emissions increase as the T falls, and therefore large amount of SO_2 are generated. The OC increases with an increase in T, with a higher T meaning that the photochemical reaction was strong, which was conducive to OC formation (Li et al., 2016, 2019).

(2) Changes with RH:

The highest OC, NO_3^- , and SO_4^{2-} concentrations were observed when RH was in the range of 80–90% (Figure 12). Under a high RH, many atmospheric heterogeneous reactions are accelerated, and the reaction products are conducive to water absorption and the deliquescence of particulate matter. They will therefore have a significant role in promoting haze formation. The coexistence of pollutant particles and fog forms a positive feedback mechanism, which will continuously promote the conversion of the gaseous pollutants discharged from the primary to secondary aerosol. This will result in their concentration continuing to increase. The SO_4^{2-} concentration in this study increased with an increase in RH. This shows the importance of the heterogeneous reactions (liquid phase reactions) under a high RH in SO_4^{2-} formation.

Unlike OC and SO_4^{2-} , more than 70–60% of the NO_3^- was produced when the RH was 50–30%. The phenomenon in which the NO_3^- concentration produced by the EP4 process (low RH) was higher than that of produced during the EP1 process (high RH) was explained in section 3.3.1. Wang et al. (2014) also reported a high NO_3^- production under a low RH. This shows that the dependence of NO_3^- on RH was not as obvious as that of SO_4^{2-} . Many studies have reported the phenomenon in which the change of the NO_3^- concentration at different RH levels in winter is much smaller than that of SO_4^{2-} (Sun et al., 2013). The NO_3^- formation was more complicated than that of SO_4^{2-} . Section 3.3.1 of this article shows that a high atmospheric oxidability, high NH_3 , high NO_2 , and high $[\text{NH}_4^+]_{\text{excess}}$ were all important in NO_3^- formation.

Compared with NO_3^- and SO_4^{2-} , RH had little effect on the changes in the OC concentration. In this study, the RH during EP4 was not high, but the OC and SOC concentrations were the highest during the whole three years (2017–2019), which was related to the high O_3 concentration, high atmospheric oxidability, and high T during this episode (see section 2.1 for details). Sun et al. (2013) reported that among the organic components, those emitted from coal combustion increased most obviously with an increase in RH. The influence of fog on SO_4^{2-} formation in winter in Beijing can be high, accounting for 70% of the overall formation, while its influence on NO_3^- was less than 30%. Our results showed that RH had the largest impact on SO_4^{2-} , followed by NO_3^- , and had the least impact on OC.

Conclusion

Based on the simultaneous observations of $\text{PM}_{2.5}$ and its chemical components at 14 sampling sites in northeast China in four severe haze pollution processes during 2017–2019, pollution formation under low T and low-sulfur coal emission conditions were analyzed. Changes in the formation and presence of the secondary pollutants SO_4^{2-} and NO_3^- under different meteorological and emission scenarios were assessed. The following conclusions were reached.

(1). The most polluted areas in northeast China were in Harbin and its surrounding suburbs and rural areas, followed by Shenyang. The most important component of $\text{PM}_{2.5}$ was OC, followed by SNA. Nitrate has surpassed SO_4^{2-} as the most important secondary inorganic component in northeast China. The main chemical components affecting haze pollution in northeast China were organic matter and inorganic water-soluble ions. The OC and EC concentrations in urban sites were high, reflecting the contribution of motor vehicles, residential heating, and combustion. The higher OC and EC concentrations in the rural sites reflect that the combustion of civilian biomass and the combustion of loose coal has become the largest source of pollutants in the suburbs and rural sites. The ratio of the two was 50.5%.

(2) The significant increase in OC, SO_4^{2-} , and NO_3^- concentrations was an important reason for haze formation. Meteorological factors such as wind direction, wind speed, T, RH, and atmospheric oxidability played an important role in secondary pollutant formation. High atmospheric oxidability was very important for NO_3^- and SO_4^{2-} formation in northeast China.

■ Nitrate formation was mainly due to the homogeneous gas-phase reactions of $\text{OH}\cdot$ with NO_2 , SO_2 , and NH_3 . The highest concentration occurred under mild winter Ts, high RH, high atmospheric oxidability (O_3 and HONO), high NH_3 concentrations, and suitable light conditions.

■ The SO_4^{2-} concentration tended to increase with an increase in vapor pressure (e^*). There were two main SO_4^{2-} formation pathways. One was the gas-phase reaction of the $\text{OH}\cdot$ oxidation of NO_2 and SO_2 . High O_3 concentrations, higher winter Ts, and high atmospheric oxidability and photochemical activity were very important for SO_4^{2-} formation during haze events. The second pathway operated under neutral or weakly alkaline conditions, during which SO_2 enters aerosol droplets, and NO_2 is more likely to react in the aqueous phase with SO_2 to increase the output of SO_4^{2-} . The difference between the SO_4^{2-} formation in northeast China and other regions was reflected by the suppression of the aqueous reaction of SO_4^{2-} due to low Ts in winter and low-sulfur coal emissions in northeast China. This resulted in the rapid generation of gas-phase oxidation processes being important for high levels of SO_4^{2-} production in the region. However, the aqueous oxidation reaction was still the most common SO_4^{2-} formation pathway in northeast China.

■ Both T and RH had an important influence on NO_3^- , SO_4^{2-} , and OC formation. The NO_3^- concentration increased with increasing T, and SO_4^{2-} concentration, with the SO_4^{2-} following a similar V-shaped pattern to that of OC. The highest NO_3^- and SO_4^{2-} concentrations occurred when the RH was 80–90%. The effect of RH on NO_3^- was not as significant as that of SO_4^{2-} , but NO_3^- formation was more complicated, being affected by multiple factors, such as RH and photochemical activity. The OC concentration increased with T, and RH had little effect on the changes in the OC concentration.

Declarations

Funding information This research was funded by the Institute of the Atmospheric Environment, China Meteorological Administration, Shenyang (2021SYIAEZD2, 2017SYIAEMS6); Scientific and Technological Research Project of Liaoning Meteorological Bureau (202012, 201502); the Institute of Atmospheric Physics, Chinese Academy of Sciences (LAPC-KF-2017-02); the Laboratory of Atmospheric Boundary Layer Physics and Atmospheric Chemistry, Special Forecast Core Business Development Projects (CMAHX20160307); the National Key R&D Program of China (2017YFC021230101);

the Natural Science Foundation of Liaoning Province (2020-MS-350), Liaoning Key Guidance Project of Research and Invention Plan(2019JH8/10300094), and the National Natural Science Foundation of China(41730647)

Compliance with ethical standards

Ethics approval and consent to participate Not applicable

Consent to Publish Not applicable

Conflict of interest The authors declare that they have no competing interests

The authors have no relevant financial or non-financial interests to disclose.

The authors have no competing interests to declare that are relevant to the content of this article.

All authors certify that they have no affiliations with or involvement in any organization or entity with any financial interest or non-financial interest in the subject matter or materials discussed in this manuscript.

The authors have no financial or proprietary interests in any material discussed in this article.

Authors are responsible for correctness of the statements provided in the manuscript.

Authors' contributions All authors contributed to the study conception and design. Material preparation, data collection and analysis were performed by Junying Sun, Yanjun Ma, Yangfeng Wang, Xiaolan Li, Yunhai Zhang, Ningwei Liu, Hujia Zhao and Deping Zhou. The first draft of the manuscript was written by Ye hong and all authors commented on previous versions of the manuscript. All authors read and approved the final manuscript.

Availability of data and materials Not applicable

Publisher's Note Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.

References

1. An JL, Li Y, Tang YJ, Chen Y, Qu Y (2014) Advances in HONO sources, HONO simulations, and the impacts of the HONO sources on regional or global air quality. *China Environmental Science* 34(2):273–281
2. Cao GL, An XQ, Zhou CH, Ren YQ, Tu J (2010) Emission inventory of air pollutants in China. *China Environmental Science* 30, 900–906.
3. Cao JJ, Wu F, Chow JC, et al. (2005) Characterization and source apportionment of atmospheric organic and elemental carbon during fall and winter of 2003 in Xi'an, China. *Atmospheric Chemistry and Physics*, 5(11): 3127–3137.
4. Chameides WL, Yu H, Liu S C, Liu M, Bergin X, Zhou L, Mearns G, Wang C S, Kiang R D, Saylor C, Luo Y, Huang A (1999) Case study of the effects of atmospheric aerosols and regional haze on agriculture, An opportunity to enhance crop yields in China through emission controls. *Proceedings of the National Academy of Sciences of the United States of America* 96(24) : 13626–13633.
5. Cheng YF, Zheng GJ, Wei C, Mu Q, Zheng B, Wang ZB, Gao M, Zhang Q, He KB, Carmichael, GR, Pöschl, U, & Su, H (2016) Reactive nitrogen chemistry in aerosol water as a source of sulfate during haze events in China. *Science Advances* 2:2375–2548.
6. Elser M, Huang RJ, Wolf R, Slowik JG, Wang Q, Canonaco F, Li G, Bozzetti C, Daellenbach KR, Huang Y, Zhang R, Li Z, Cao J, Baltensperger U, El-Haddad I, & Prévôt AS (2015) New insights into PM 2.5 chemical composition and sources in two major cities in China during extreme haze events using aerosol mass spectrometry. *Atmospheric Chemistry and Physics* 15: 3207–3225.
7. Finlayson-Pitts BJ, Wingen LM, Sumner AL, Syomin D, & Ramazan KA (2003) The heterogeneous hydrolysis of NO₂ in laboratory systems and in outdoor and indoor atmospheres: An integrated mechanism. *Physical Chemistry Chemical Physics* 5: 223–242.
8. Ge X, Zhang Q, Sun Y, Ruehl CR, & Setyan A (2012) Effect of aqueous-phase processing on aerosol chemistry and size distributions in Fresno, California, during wintertime. *Environmental Chemistry* 9: 221–235.
9. Tang G, Bo H, Wang L, Ji D, Wang Y, & Liu Z, et al. (2014). Researching significance, status and expectation of haze in Beijing-Tianjin-Hebei region. *Advances in Earth Science*, 29(3), 388–396.
10. Guo H, Weber RJ, & Nenes A (2017) High levels of ammonia do not raise fine particle pH sufficiently to yield nitrogen oxide-dominated sulfate production. *Scientific Reports* 7.
11. Harris E, Sinha B, van Pinxteren D, Tilgner A, Fomba KW, Schneider J, Roth A, Gnauk T, Fahlbusch B, Mertes SC, Lee T, Collett JL, Foley SP, Borrmann S, Hoppe P, & Herrmann H, (2013) Enhanced Role of Transition Metal Ion Catalysis During In-Cloud Oxidation of SO₂. *Science* 340: 727 - 730.
12. Han LH, Chen YY, Jia L, et al. (2014). Heterogeneous reactions of NO₂ on MgO particle surfaces. *Science China Chemistry*, 44(12):2004–2012.
13. He L, Hu M, Huang X, Yu B, Zhang Y, & Liu D (2004) Measurement of emissions of fine particulate organic matter from Chinese cooking. *Atmospheric Environment* 38, 6557–6564.

14. Hong Y, Ma Y, Sun J, Li C, Zhang Y, Li X, Zhou D, Wang Y, & Liu N (2019) Water-soluble ion components of PM₁₀ during the winter-spring season in a typical polluted city in northeast China. *Environmental Science and Pollution Research* 26: 7055-7070.
15. Hu WW, Hu M, Deng ZQ, Xiao R, Kondo Y, Takegawa N, Zhao YJ, Guo S, Zhang YH (2012) The characteristics and origins of carbonaceous aerosol at a rural site of PRD in summer of 2006. *Atmospheric Chemistry and Physics* 12: 1811-1822.
16. Hu YQ, Ma ZH, Feng YJ, Wang C, Chen YY, He M (2015) Emission characteristics of water-soluble ions in fumes of coal fired boilers in Beijing. *Environmental Sciences* 36(6):1966–1974.
17. Huang X, Liu Z, Zhang J, Wen T, Ji D, & Wang Y (2016) Seasonal variation and secondary formation of size-segregated aerosol water-soluble inorganic ions during pollution episodes in Beijing. *Atmospheric Research* 168: 70-79.
18. Ji D, Gao W, Zhang J, Morino Y, Zhou L, Yu P, Li Y, Sun J, Ge B, Tang G, Sun Y, & Wang Y, (2016) Investigating the evolution of summertime secondary atmospheric pollutants in urban Beijing. *The Science of the total environment* 572: 289-300 .
19. Li C, Bosch Carme, Kang SC, et al., 2016. Sources of black carbon to the Himalayan–Tibetan Plateau glaciers. *Nature Communications*, 7: 12574.
20. Li C, Han XW, Kang SC, et al.(2019) Heavy near-surface PM_{2.5} pollution in Lhasa, China during a relatively static winter period. *Chemosphere*, 214: 314-318.
21. Li H, Duan F, Ma Y, He K, Zhu L, Ma T, Ye S, Yang S, Huang T, & Kimoto T (2018a) Haze pollution in winter and summer in Zibo, a heavily industrialized city neighboring the Jing-Jin-Ji area of China: source, formation, and implications. *Atmospheric Chemistry and Physics* :1-40.
22. Li J, Du H, Wang Z, Sun Y, Yang W, Li J, Tang X, & Fu P (2017) Rapid formation of a severe regional winter haze episode over a mega-city cluster on the north China Plain. *Environmental pollution* 223: 605-615 .
23. Li L, Hoffmann MR, & Colussi AJ (2018b) Role of nitrogen dioxide in the production of sulfate during Chinese haze-aerosol episodes. *Environmental science & technology* 52(5): 2686-2693 .
24. Li YH, Duan JC, Zheng NJ, Zheng NJ, Tan JH, Rao ZG, Ma YL, He KB (2015) Characteristics of organic and element carbon in fine particles in Lanzhou. *Journal of University of Chinese Academy of Sciences* 32(4) : 490-497
25. Liu X, Sun K, Qu Y, Hu M, Sun Y, Zhang F, & Zhang Y (2015) Secondary formation of sulfate and Nitrate during a haze episode in megacity Beijing, China. *Aerosol and Air Quality Research* 15: 2246-2257.
26. Luo L, Zhu R, Song C, Peng J, Guo W, Liu Y, Zheng N, Xiao H, & Xiao H (2021) Changes in nitrate accumulation mechanisms as PM_{2.5} levels increase on the north China Plain: A perspective from the dual isotopic compositions of nitrate. *Chemosphere* 263: 127915 .
27. Pathak RK, & Chan CK (2005) Inter-particle and gas-particle interactions in sampling artifacts of PM_{2.5} in filter-based samplers. *Atmospheric Environment* 39: 1597-1607.
28. Pathak RK, Wu W, & Wang T (2008) Summertime PM_{2.5} ionic species in four major cities of China: nitrate formation in an ammonia-deficient atmosphere. *Atmospheric Chemistry and Physics* 9: 1711-1722.
29. Schauer JJ, Kleeman MJ, Cass GR, & Simoneit BR (2002) Measurement of emissions from air pollution sources. 5. C1-C32 organic compounds from gasoline-powered motor vehicles. *Environmental science & technology* 36(6): 1169-80 .
30. Seinfeld JH, Pandis SN (2006) Atmospheric chemistry and physics: from air pollution to climate change, seconded. John Wiley & Sons, New York.
31. Shi Y, Chen JM, Hu DW, Wang L, Yang X, Wang XM (2014) Airborne submicron particulate (PM₁) pollution in Shanghai, China: Chemical variability, formation/dissociation of associated semi-volatile 734 components and the impacts on visibility. *Science of the Total Environment* 473: 199-206.
32. Shi XR (2019) Study on the relationship between atmospheric aerosol pH and secondary nitrate based on online observed data. Nankai University.
33. Sobhani N, Kulkarni S, and Carmichael G R (2018) Source sector and region contributions to black carbon and PM_{2.5} in the Arctic, *Atmospheric Chemistry and Physics* 18: 18123–18148.
34. Sun Y, Chen C, Zhang Y, Xu W, Zhou L, Cheng X, Zheng H, Ji D, Li J, Tang X, Fu P, & Wang Z (2016) Rapid formation and evolution of an extreme haze episode in northern China during winter 2015. *Scientific Reports*, 6.
35. Sun YL (2018) Vertical structures of physical and chemical properties of urban boundary layer and formation mechanisms of atmospheric pollution. *Chinese Science Bulletin* 63: 1374-1389.
36. Sun YL, Wang Z, Dong H, Yang T, Li J, Pan X, Chen P, & Jayne JT (2012) Characterization of summer organic and inorganic aerosols in Beijing, China with an aerosol chemical speciation monitor. *Atmospheric Environment* 51: 250-259.
37. Sun YL, Wang Z, Fu P, Jiang Q, Yang T, Li J, & Ge X (2013) The impact of relative humidity on aerosol composition and evolution processes during wintertime in Beijing, China. *Atmospheric Environment* 77: 927-934.
38. Tan JH, Duan JC, Chen DH et al (2009) Chemical characteristics of haze during summer and winter in Guangzhou. *Atmospheric research*, 94(2):238–245.
39. Tang XY, Zhang YH, Shao M (2006) Atmospheric environmental chemistry second edition. Higher Education Press.
40. van Donkelaar A, Martin RV, Brauer M, Hsu NC, Kahn RA, Levy RC, Lyapustin AI, Sayer AM, & Winker DM (2016) Global estimates of fine particulate matter using a combined geophysical-statistical method with information from satellites, models, and monitors. *Environmental science & technology* 50 7: 3762-3772 .

41. Wang C, Cao JY, Duan XL, Chen H, Yan YL, Peng L (2021a) Characteristics and sources analysis of carbonaceous components in PM_{2.5} in winter in four cities of Shanxi province. *Environmental Engineering* 39(06):114-121.
42. Wang G, Zhang R, Gómez ME, Yang L, Levy Zamora M, Hu M, Lin Y, Peng J, Guo S, Meng J, Li J, Cheng C, Hu T, Ren Y, Wang Y, Gao J, Cao J, An Z, Zhou W, Li G, Wang J, Tian P, Marrero-Ortiz W, Secrest J, Du Z, Zheng J, Shang DJ, Zeng L, Shao M, Wang W, Huang Y, Wang Y, Zhu Y, Li Y, Hu J, Pan B, Cai L, Cheng Y, Ji Y, Zhang F, Rosenfeld D, Liss PS, Duce RA, Kolb CE, & Molina MJ (2016a) Persistent sulfate formation from London fog to Chinese haze. *Proceedings of the National Academy of Sciences* 113: 13630 - 13635.
43. Wang H, Lu K, Chen X, Zhu Q, Wu Z, Wu Y, & Sun K (2018) Large particulate nitrate formation from N₂O₅ uptake in a chemically reactive layer aloft during winter time in Beijing. *Atmospheric Chemistry and Physics* 1-27.
44. Wang Y S, Zhang JK, Wang LL, et al.(2014) Researching significance—status and expectation of haze in Beijing-Tianjin-Hebei region. *Advances in Earth Science*.29(3): 388-396.
45. Wang W, Liu M, Wang T, Song Y, Zhou L, Cao J, Hu J, Tang G, Chen Z, Li Z, Xu Z, Peng C, Lian C, Chen Y, Pan Y, Zhang Y, Sun Y, Li W, Zhu T, Tian H, & Ge M (2021b) Sulfate formation is dominated by manganese-catalyzed oxidation of SO₂ on aerosol surfaces during haze events. *Nature Communications* 12(1), 1-10.
46. Wang XQ, Zhou Y, Cheng SY, Wang G (2016b) Characterization and regional transmission impact of water-soluble ions in PM_{2.5} during winter in typical cities. *China Environmental Science* 36(08):2289-2296.
47. Xu H, Chen JQ, He DT, Cheng P, Wang W, Zhu L, Yang, H, Gu ZQ (2017a) Climatic characteristics of haze weather during heating periods from 1980 to 2015 at Shenyang region (in Chinese). *Journal of Meteorology and Environment* 33(2):87–94.
48. Xu J, Xu, M Snape CE, He J, Behera SN, Xu H, Ji D, Wang C, Yu H, Xiao H, Jiang Y, Qi B, & Du R (2017b) Temporal and spatial variation in major ion chemistry and source identification of secondary inorganic aerosols in northern Zhejiang Province, China. *Chemosphere* 179: 316-330 .
49. Yang L, (2018) Analysis of Pollution Characteristics of EC/OC in PM_{2.5} in Changchun City. Jilin University.
50. Zhang J, Liu L, Xu L, Lin Q, Zhao H, Wang Z, Guo S, Hu M, Liu D, Shi Z, Huang D, & Li W, (2020) Exploring wintertime regional haze in northeast China: role of coal and biomass burning. *Atmospheric Chemistry and Physics* 20: 5355-5372.
51. Zhang Y, Shao M, Zhang Y, Zeng L, He L, Zhu B, Wei Y, & Zhu X (2007). Source profiles of particulate organic matters emitted from cereal straw burnings. *Journal of environmental sciences* 192: 167-75 .

Figures

Figure 1

Locations of the 14 sampling sites in northeast China

Figure 2

The average concentrations of PM_{2.5} and its chemical components at each sampling site (Note: There are three columns for each sampling site, representing 2017, 2018, and 2019 respectively).

Figure 3

The concentrations of PM_{2.5} and its chemical components (OC, SO₄²⁻, and NO₃⁻: μg·m⁻³)

Figure 4

Temporal changes in the concentrations of PM₁₀, PM_{2.5}, and their chemical components and their ratios in PM_{2.5}, as well as the variations in gaseous emissions, meteorological conditions, and the boundary layer height (BLH) in EP1–EP4

Figure 5

Time series of the wind direction and wind speed at the main sampling sites

Figure 6

The PM_{2.5} concentration and a wind field diagram for EP3, showing the jump point of the PM_{2.5} concentration

Figure 7

The PM_{2.5} concentration and corresponding wind field on February 28, 2019 in EP4

Figure 8

The relationship between [NH₄⁺]excess and NO₃⁻ and NO₃⁻+Cl⁻. (a) The relationship between [NH₄⁺]excess and NO₃⁻, with the different colors indicating different pollution processes; (b) the relationship between [NH₄⁺]excess and NO₃⁻+Cl⁻, with the different colors indicating different pollution processes; (c) the colors indicate different levels of relative humidity (RH); and (d) the colors indicate different temperatures (Ts).

Figure 9

The NO₃⁻ and SO₄²⁻ concentrations and their precursor gases at the SY site

Figure 10

The relationships between SO₄²⁻ and the sulfur oxidation rate (SOR), ambient water vapor pressure(e^*), relative humidity (RH), and temperature (T)

Figure 11

The statistical values of various pollutants, relative humidity (RH), and temperature (T) in four areas divided by the SO_4^{2-} concentration and ambient water vapor pressure (e^*)

Figure 12

Diffraction pattern of the diurnal variation of the proportional contents of several important chemical components of $\text{PM}_{2.5}$