The heaviest particulate air-pollution episodes occurred in northern China in January, 2013: Insights gained from observation

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HIGHLIGHTS

- The obvious decline in air quality was found in Beijing in January.
- The highest hourly PM\textsubscript{2.5} concentrations reached approximately 1000 \(\mu\)g/m\textsuperscript{3}.
- More secondary particles were observed during severe air pollution episodes.

ARTICLE INFO

Article history:
Received 11 February 2014
Received in revised form 21 April 2014
Accepted 23 April 2014
Available online 26 April 2014

Keywords:
Air pollution episodes
PM\textsubscript{2.5}
PM\textsubscript{1}
Sulfate
Nitrate
OC
EC

ABSTRACT

A comprehensive measurement was conducted to analyze the heaviest air pollution episodes, which occurred in January 2013 with the focus on particulate characterization and haze. Based on observation, five heavy pollution episodes were recorded, whose frequencies are far greater than in other years. Among the heavy pollution episodes, two distinct severe regional PM\textsubscript{2.5} (particulate matter (PM) with an aerodynamic diameter \(\leq 2.5\ \mu\)m) pollution episodes were selected for investigation. One episode is characterized by an explosive growth in PM\textsubscript{2.5} concentrations within several hours, which is mainly caused by the high local emission under stagnant conditions; the other episode is characterized by four-day consecutive increases in PM\textsubscript{2.5} concentrations, which is largely attributed to a combination of slow regional transport and local accumulation. The PM compositions and concentrations including PM\textsubscript{2.5}, PM\textsubscript{1} (PM with an aerodynamic diameter \(\leq 1\ \mu\)m), nitrate, sulfate, ammonium, organic carbon (OC) and elemental carbon (EC) as well as main gaseous precursor concentrations are analyzed in Beijing during the two episodes. Rapid gas-to-particle conversion, coagulation and collision of particles are discussed under high emission and stagnant weather conditions. High sulfur and nitrogen oxidation ratios were found, suggesting that additional production of sulfate and nitrate occurred during the pollution episodes. In addition, high levels of secondary particles were transported from surrounding regions via vertical mixing and horizontal transport during the polluted days. Notably, the stationary source is still a major contributor to the pollution episodes. Clear evidence is presented indicating that the secondary formation of particulate was one important mechanism in the formation of the heavy pollution episodes. To control the air pollution effectively, more stringent restriction measures on the SO\textsubscript{2} and NO\textsubscript{x} emissions should be strictly executed at the regional scale.

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1. Introduction

Northern China has experienced rapid economic growth over the past two decades accompanied by the development of large-scale industries and urbanization. This economic boom has led to a general decline in air quality in urban agglomerations (Shao et al.,...
Serious air-pollution problems frequently occur, such as high concentrations of PM accompanying haze, which has attracted widespread attention (Molina and Molina, 2004; He et al., 2011) because exposure to airborne PM could result in adverse effects on public health (Fann and Risley, 2013). In addition, the radiative budget is affected by high PM loadings, which contribute to global climate change (IPCC, 2007). Moreover, some studies showed that the serious particulate air pollution generated over eastern Asia can be transported to the western Pacific Ocean region (Jo and Kim, 2013). It is evident that the impact on air quality due to the long-range transport is expected to increase in downstream regions (Lin et al., 2014).

In January 2013, five hazardous air-pollution episodes occurred, which were considered the most serious pollution events since 2000 (with the exception of dust episodes). These episodes led to the cancellations of hundreds of flights, warnings to avoid all outdoor activities and a spike in respiratory disease cases. Although the domestic and foreign media have reported the severity of this episode and emergent response measures for air pollution, a scientific and professional analysis of these episodes is necessary to recognize the evolving process of air pollution and to evaluate the rationality of instituting policy.

To date, serious PM-pollution episodes have been reported in a large number of studies, including in situ observations and air pollution-monitoring campaigns conducted by research institutions (Fu et al., 2008; Huang et al., 2012). The results showed that regional emissions and weather patterns play important roles in the PM$_{10}$ (PM with an aerodynamic diameter $\leq$ 10 $\mu$m) and PM$_{2.5}$ pollution over a region (He et al., 2011). OC, EC, sulfate, nitrate and ammonium have been found to comprise the major fraction of fine particles. The sources of PM mainly include secondary inorganic species, coal combustion, vehicle exhaust, biomass burning, and mineral dust, depending on the seasons and sites. However, each PM pollution episode has its own unique characteristics. Recognizing the characteristics of each severe PM pollution episode and understanding the causes of these episodes are a prerequisite for authorities and researchers to effectively reduce air pollution. The main challenge for recognizing the characteristics of PM pollution episodes is the identification of the contributions of local emission as well as the long-range transport and linkage of the emissions of PM and its precursors with the transport, transformations and fate of PM under the high emission scenario.

Under the above-mentioned background, this paper will present an in-depth explanation of how local emissions and regional transport differently influence the compositions and concentrations of PM. The evolutions of episodes in different size-segregated PM (PM$_1$ and PM$_{2.5}$) are also described with the high temporal resolution measured chemical species. Knowledge of the rapid evolution processing of PM components is obtained. This study provides clear evidence that the effective management of air pollution requires collaboration among local, regional and state authorities in northern China.

2. Description of the experiment

2.1. Measurement site

The study was conducted using an air quality observation network constructed by the Institute of Atmospheric Physics, Chinese Academy of Sciences, in northern China. Fig. 1 and Table 1 show the locations of these air quality monitoring stations. All the air quality monitoring stations were selected and set up according to the United States Environmental Protection Agency method designation (US EPA, 2007).

Fig. 2 and Table 1 show the location of the study sites in Beijing. The sites include Tiantan Park, Olympic Community in the Dongcheng District (QC), Wanshouxigong Park (WP), Guanyuan park (GP), Shijiazhuang (SJZ), and Huairou (HR). The results showed that regional emissions and weather patterns play important roles in the PM$_{10}$ (PM with an aerodynamic diameter $\leq$ 10 $\mu$m) and PM$_{2.5}$ pollution over a region (He et al., 2011). OC, EC, sulfate, nitrate and ammonium have been found to comprise the major fraction of fine particles. The sources of PM mainly include secondary inorganic species, coal combustion, vehicle exhaust, biomass burning, and mineral dust, depending on the seasons and sites. However, each PM pollution episode has its own unique characteristics. Recognizing the characteristics of each severe PM pollution episode and understanding the causes of these episodes are a prerequisite for authorities and researchers to effectively reduce air pollution.

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![Fig. 1. A map showing the location of the study sites and topography in northern China.](Image)
Xinyunali (XYL), North Fifth Ring (NFR), IAP, Miyuan (MY), Huairou (HR), Changping (CP), Shunyi (SY), Haidian (HD), Ling Mountain (background site, LM), Shijingshan (SJS) and Tongzhou (TZ).

2.2. Instruments

The set-up of the instruments, their precision and accuracy, their operation and maintenance, calibration methods and scheduled procedures of quality assurance and control have previously been described in detail (Ji et al., 2008, 2012). Briefly, commercial instruments from Thermo Fisher Scientific (TE), USA were used to measure O3 (model 49I), NO/NO2/NOx (model 42I), CO (model 48I) and SO2 (model 43I). The analyzers of SO2, NOx and CO were calibrated using a 50 ppmv SO2 standard gas, a 52 ppmv NO standard gas and a 5000 ppmv CO standard gas (Scott-Marin gases, Riverside, CA, USA), respectively. An O3 calibrator (49C PS) was used to calibrate the O3 analyzers. The calibrator is traceable to the National Institute of Standards and Technology in USA. In addition, the CO analyzer was zeroed every two hours using an internal catalytic converter. PM2.5 and PM10 were measured with a tapered-element oscillating microbalance method (R&P TEOM 1405DF, USA) or a beta-attenuation method (Metone BAM-1020, USA). Meteorological parameters were also measured in Beijing, including wind, temperature, relative humidity and total solar radiation, using Automatic Weather Stations (Model milos-520, Vaisala, Finland).

A Partisol 2025i Sequential Air Sampler (TE, MA, USA) equipped with multiple cassettes was used to collect ambient PM2.5 on a building roof 8 m above ground at IAP. Quartz fiber filters (47 mm diameter; Pall Life Sciences, Ann Arbor, MI, USA) were used to collect samples. The filters were sampled for 12-h periods during ambient air sampling. All the filters were heat-treated at 900 °C for at least 4 h for cleaning prior to filter sampling. The flow rates were set at 16.7 L/min during sampling. The OC and EC values were determined using a thermal/optical reflectance protocol using a DRI model 2001 carbon analyzer (Atmoslytic, Inc., Calabasas, CA, USA). The particulate chloride, nitrate, sulfate, ammonium and potassium in the fine fractions were analyzed within 24 h at the laboratories using ion chromatography (using a Dionex DX 120 connected with a DX A550 auto-sampler for anions and a DX ICS90 connected with a DX A540 auto-sampler for cations).

A High-Resolution Time-of-Flight Aerosol Mass Spectrometer (HR-ToF-AMS) manufactured by Aerodyne Research Inc. (Billericia, MA, USA) in urban Beijing was used to measure airborne submicron particles and its chemical components during this month of serious pollution. Detailed information on the HR-ToF-AMS has been reported by Zhang et al. (2014).

Chloride, nitrate, sulfate, ammonium and potassium in PM2.5 were observed every hour using the Rapid Collector of Particles-Ion Chromatography System (RCFP-IC). Detailed information on RCFP-IC has been reported by Wen et al. (2006).

2.3. Trajectories calculation

The trajectories were calculated using Trajstat, which is available on the website of the National Oceanic and Atmospheric Administration (NOAA)’s Air Resources Laboratory. The 48-h trajectories were calculated terminating at 6:00 UTC at the height of 500 m and then statistically analyzed. Matrix trajectories were calculated using the Web version of the Hybrid Single Particle Lagrangian Integrated Trajectory model, which is available on the website of the NOAA’s Air Resources Laboratory. The 48-h matrix trajectories were calculated terminating at 0:00 UTC (matrix points 37°, 39°, 41° N by 114°, 116°, 118°, 120° E) for 48-h intervals at the height of 500 m.

3. Results and discussion

3.1. Variations in PM2.5 on January of 2011, 2012 and 2013

As shown in Fig. 2, the average concentrations of PM2.5 were 43 ± 53, 111 ± 131 and 199 ± 152 µg/m³ in January of 2011, 2012 and 2013, respectively. The exceedance days of the World Health Organization (WHO) air quality threshold value of PM2.5 (35 µg/m³) are 14, 28 and 31, respectively. These results suggested that the air quality had worsened in Beijing. This worsened air quality was related with the increase in the total volumes of industrial production and consumer goods (volumes of industrial production and consumer goods as a proxy for the anthropogenic emission) and southern and stagnant air masses arriving in Beijing (Fig. 3), i.e., more polluted air mass dominating the study area in January 2013. Additionally, local meteorological factors (Table 2) favored the accumulation and hygroscopic growth of PM (Flores et al., 2012). In detail, northern China experienced extreme temperature-dropping events, and part of northern China even experienced snow storms during December 2012. The ground was partly covered with snow in northern China. When the atmospheric temperature increased, this snow would have provided ample water vapor near the ground. This vapor provided the basis for the formation of haze/fog during January 2013. Moreover, a sudden stratospheric warming (SSW) (Fig. 4) occurred, keeping the stratosphere warm for several weeks starting from January 5, 2013. Anomalous features extended well into the troposphere, impacting the surface for much of January 2013. These led to abrupt slow-downs in the drastic decreasing temperatures caused by the polar night and the reversed direction of westerly winds of the polar vortex in the Northern Hemisphere. This change is not conducive to the
recirculation of the polar vortex and forces the polar vortex to weaken. During the course of the rotation and collapse, a weakened polar vortex in northern Asia occasionally carried weak cold air to the eastern regions of China. Positive anomalies of the atmospheric temperature and relative humidity were found, which indicated that the temperature and relative humidity were warmer and wetter than normal. Low wind on the surface occurred concurrently with these synoptic systems. Note that it is sunny at the altitude of approximately 1 km in eastern China (Guan and He, 2013). However, the solar radiation could not pass through the layer of haze. It is not conducive to the diffusion of air pollutants. At the same time, the saturation of water vapor is reached at surface. These meteorological conditions were more favorable for the formation of high PM pollution accompanying haze. The sunshine duration also decreased year by year. The increase in anthropogenic emission accompanying the unfavorable meteorological situations resulted in temporal variations in PM in Beijing year by year. Notably, serious high PM pollution accompanying haze gives the positive feedback to unfavorable diffusion conditions, and vice versa.

3.2. Variations in PM2.5 and its relevant gases during the episodes in January 2013

3.2.1. Variations in PM2.5 during the episodes in January 2013

Fig. 5 shows that severe PM pollution episodes were recorded in the selected cities of northern China in January 2013. In this paper, two severe PM2.5 pollution episodes were selected for investigation. One of the recorded episodes (E1) showed an explosive growth in the PM2.5 concentrations within a few hours, while the other episode (E2) showed continuous increase in the PM2.5 concentrations over approximately five days.

E1: As shown in Fig. 6, the hourly mean concentrations of PM2.5 started to increase at 11:00 on January 12, reaching peak concentrations at approximately 16:00 on January 12 at nearly all of the monitoring sites in Beijing. This observation suggested that the same synoptic system almost dominated all the sites of Beijing. However, the background PM2.5 levels were substantially lower than the corresponding higher concentrations measured at the urban sites. The difference in the PM2.5 concentrations between at the IAP site and at the background site is, approximately 450 μg/m³. The local sources were therefore mainly responsible for the high concentrations. This result was in accordance with the urban PM2.5 excess caused by emission from local sources, which produced sharper spatial gradients of PM2.5 (Ji et al., 2012). Meteorologically, the relative humidity were high (75–85%), the thickness of the inversion layer ranged from 500 to 1000 m, and the strength of the temperature inversion varied between 5 and 10 °C. Specifically, the mixing layer height only ranged from 200 to 300 m (sunny day for 2000–3000 m). For the regional scale, the daily average concentrations far exceeded the Chinese Grade II standard (75 μg/m³) and even attained hazardous levels (300 μg/m³) in Xianghe and Shijiazhuang on January 12. Hourly maximum values of approximately 1000 μg/m³ were recorded by the PM10 monitor with a beta-attenuation method in Beijing and Shijiazhuang, which are the highest values reported in China, with the exception of values recorded during dust episodes. During the same period, the
maximum hourly PM$_{2.5}$ values published by Ministry of Environmental protection (MEP) at the Xizhimen site, the South Third Ring Road site and the Tongzhou site (Fig. 1) in Beijing also reached approximately 1000 $\mu$g/m$^3$. These results suggest that northern China suffers from very serious PM pollution. The PM$_{2.5}$ concentrations measured in our study are lower than those observed in the eruption of Eyjafjallajökull on Iceland during 2010 (Volker et al., 2012), but the maximum concentration of PM$_{2.5}$ and the severity of episodes in Beijing have exceeded recent records in New Delhi (Times of India, 2013), which is one of the most polluted areas in the world (Shweta et al., 2013). Elevated PM$_{2.5}$ levels were also measured at the background station of Xinglong and at the rural station of Yucheng. The maximum daily mean concentrations were 171 and 327 $\mu$g/m$^3$, respectively, which were far below the corresponding concentrations measured at the urban sites. This result also indicated that the local sources were responsible for the high PM$_{2.5}$ concentrations during E1. In addition, the data recorded by MEP (Fig. 7) showed that the daily PM$_{2.5}$ concentrations exceeded 350 $\mu$g/m$^3$ in the main cities of Hebei province, including Baoding (BD), Cangzhou (CZ), Handan (HD), Hengshui (HS), Langfang (LF), Shijiazhuang (SJZ), Tangshan (TS) and Xingtai (XT) on January 12, 2013.
E2: As shown in Figs. 5 and 8, the daily mean concentrations of PM$_{2.5}$ began to increase on January 25, reaching peak concentrations on January 29 at almost all of the monitoring sites. With the exception of the Xinglong site, the daily mean PM$_{2.5}$ concentrations exceeded the Chinese Grade II standard at all of the sites from the beginning of January 27. The highest daily mean PM$_{2.5}$ concentrations were 502, 351, 257, 202, 200 and 80 $\text{mg/m}^3$ at the Shijiazhuang, Beijing, Yucheng, Xianghe, Tianjin and Xinglong sites, respectively.

As shown in Fig. 9, during E2 the trajectories terminating at (37°, 116°), (37°, 118°), (37°, 120°), (39°, 116°) and (39°, 118°) originated from the south of North China Plain with short pathways and obvious curves, which were favorable for the transport and the continuous accumulation of PM$_{2.5}$, the formation of regional haze and the generation of regional air-pollution episodes. Regarding the spatial variations of PM$_{2.5}$ in Beijing (Fig. 8), the PM$_{2.5}$ concentrations in urban sites were similar with those in suburban, rural or background sites. Specially, the values measured at the background site were even higher than those measured at the urban site covered with numerous plants. These results indicate that the elevated concentrations prevailed over a region and did not solely originate from urban sources in Beijing. Regional transport played an important role in the regional PM$_{2.5}$ concentrations.

3.2. Variations in trace gases during the episodes on January 2013

Fig. 5 also shows the trace gases measured at the sites over the entire study period. The highest or elevated mean values of NO$_x$ and CO occurred at the time of the PM$_{2.5}$ peak, while the average O$_3$ concentration reached zero, except at the Xinglong site, during the study period. During high-pollution days, the NO$_2$ concentrations exceeded the national II standard (daily mean 120 $\mu$g/m$^3$) at the Beijing, Shijiazhuang and Xinglong sites, and the maximum hourly NO$_2$ level (760 $\mu$g/m$^3$) was found in Shijiazhuang. SO$_2$ is emitted into the atmosphere by the combustion of fossil fuels containing sulfur (in particular, coal and heavy fuel oil), while a minor source of SO$_2$ is road transport, which is important in some urban areas, especially alongside busy roads. The hourly maximum SO$_2$ level, 673 $\mu$g/m$^3$, was found in Shijiazhuang. Surprisingly, the highest SO$_2$ concentrations were not observed on the most polluted days. This pattern suggests that the stable weather conditions during this time were favorable for the conversion of SO$_2$ to sulfate. CO showed a similar variation trend as PM$_{2.5}$. The hourly maximum CO level, 16.1 mg/m$^3$, was found in Shijiazhuang. Values exceeding the Chinese Grade II standard of CO (daily mean of 4 mg/m$^3$) were found in Beijing, Shijiazhuang, Tianjin and Xinglong on January 12 and were found in Beijing, Shijiazhuang and Xinglong on January 29. These high levels corresponded to large volumes of vehicle traffic or low exhaust-emission standards in the above areas.

3.3. Chemical characteristics of PM$_1$ and PM$_{2.5}$ during the episodes on January 2013, taking Beijing for example

Fig. 10 presents the variations of the OC and EC components in PM$_{1}$ and PM$_{2.5}$. During E1, a very high concentration of OC was observed. Of all the components, the OC concentrations increased the most rapidly. Higher OC concentrations in Beijing have been reported during the winter because of the complex energy structures used for heating and cooking (Sun et al., 2013). The rapid increase in the OC concentrations was caused by both local emission and secondary formation during E1. EC shows the similar variations with OC. The correlation coefficients between OC and EC in PM$_{2.5}$ and PM$_{1}$ were 0.89 and 0.92 ($p < 0.0001$), suggesting that the OC and EC originate from similar emission sources. The main source contributing to E1 was a mixture of vehicle exhaust, cooking and coal burning in winter via the ratios of OC/EC. In addition, the OC/EC ratio in PM$_{2.5}$ is used to characterize the presence of secondary organic PM when the value exceeds 2.0 (Chow et al., 1996). The OC/EC ratio was lower than 2.0 on non-episode days but significantly increased to 6.2 during E1, which suggested that the secondary formation of organic particles had a greater impact. The
Secondary organic carbon (SOC) is estimated using the following equation (Chow et al., 1996):

\[
SOC = \frac{OC}{POC}
\]

\[
POC = EC \times \left(\frac{OC}{EC}_{\text{prim}}\right)
\]

where OC is the measured total OC. The primary organic carbon (POC) could be calculated from the formula \(EC \times \left(\frac{OC}{EC}_{\text{prim}}\right)\), where \(\left(\frac{OC}{EC}_{\text{prim}}\right)\) was represented by the observed minimum ratio \(\left(\frac{OC}{EC}\right)_{\text{min}}\), and assumptions regarding the use of this procedure were discussed in detail by Castro et al. (1999). The highest SOC concentrations, 130 µg/m³, indicated that the secondary formation of PM was one important mechanism in the formation of the heavy pollution episode. Biomass-burning emissions are generally characterized by the content of water-soluble K⁺ (Hosseini et al., 2010). The K⁺/OC ratio can therefore be used to distinguish biomass burning from other sources of OC. In this study, the K⁺/OC ratio ranged from 0.01 to 0.08 in PM₂.₅ and PM₁. A poor correlation between OC and K⁺ was observed in PM₂.₅ and PM₁. Therefore, biomass burning contributed less to carbonaceous PM during E₁, whereas domestic charcoal combustion contributed considerably to the high PM loading.

The main water-soluble ionic concentrations of PM₂.₅ were found in the order \(\text{SO}_4^{2-} > \text{NO}_3^- > \text{NH}_4^+ > \text{Cl}^- > \text{K}^+\) during E₁. The ionic concentrations of PM₁ were also in this order. The concentrations of total water-soluble inorganic ions accounted for 42.1 ± 3.9% for PM₂.₅ and 51.0 ± 5.0% for PM₁. The results indicated...
that the percent of water-soluble ionic species in PM$_{2.5}$ was lower than that in PM$_{1}$. The levels of ions in PM$_{1}$ accounted for 57.7 ± 5.0% with the major ions being SO$_4^{2-}$, NO$_3^-$ and NH$_4^+$. Of these ions, SO$_4^{2-}$ contributes to 20.7 ± 2.4 and 25.3 ± 3.9% of the sampled mass in PM$_{2.5}$ and PM$_{1}$, respectively. The highest hourly SO$_4^{2-}$ concentrations are 185 and 74 mg/m$^3$ in PM$_{2.5}$ and PM$_{1}$ samples, respectively, which indicates the additional production of sulfate mass during high PM episodes. Non-sea-salt sulfate is generally produced by the oxidation of SO$_2$, whose conversion to sulfate depends on the concentrations of precursor gases and oxidants and on meteorological conditions such as temperature and relative humidity. To infer the degree of atmospheric transformation of SO$_2$ to SO$_4^{2-}$, the sulfur oxidation ratio (SOR) was calculated. The SOR is defined as follows: SOR = (n-SO$_4^{2-}$)/(n-SO$_4^{2-}$ + n-SO$_2$). The average SOR values are 0.55 ± 0.20 and 0.47 ± 0.18 in PM$_{1-2.5}$ (PM with an aerodynamic diameter between 1 and 2.5 μm) and PM$_{1}$, respectively. The increase of additional sulfate mass is likely from aqueous production rather than photochemical production because of low ozone concentrations (Sun et al., 2013). As shown in Fig. 11, the peak SO$_2$ concentrations occurred when the planetary boundary layer (PBL) rapidly developed. This result suggested that the higher concentrations of SO$_2$ at the high altitude, which originated from elevated point sources or regional transport, can be exchanged towards the ground, leading to the increase in the near-surface high SO$_2$ concentrations. With the decay of the PBL, SO$_2$ is capped on the surface and rapid conversion of SO$_2$ to sulfate occurred, which resulted in the increase in the sulfate concentrations and the decline in the SO$_2$ concentrations. Ammonia sulfate, which has a low vapor pressure, is one of the most important sulfate particles. Usually, one mole sulfate will remove two mole ammonia from the gas phase to form (NH$_4$)$_2$SO$_4$ before ammonia is available for further reactions. The system is divided into two regimes based on the ratio of [A]/[S], defining the total amounts of sulfate [S], nitrate [N], and ammonium [A]. One is ammonia-poor regime ([A]/[S] < 2):
the other is ammonia-rich regime \([\text{[A]}/\text{[S]} > 2]\). The ratios of \([\text{[A]}/\text{[S]}\) in both PM1 and PM2.5 are lower than 2 during E1. This result suggested that there is not a sufficient amount of NH3 to neutralize the available sulfate, which will tend to drive nitrate to the gas phase due to the thermo-dynamical instability of ammonium nitrate. In addition, a new mechanism is found in which high concentrations of NO2 promote the conversion of SO2 to SO4\(^{2-}\) (He et al., 2014). Considering aforementioned results, the competing system of NH4\(^+\)–NO3\(^−\)–SO4\(^{2-}\) is one important contributor to high PM pollution episode.

NO3\(^−\) contributes to 11.9 ± 0.4 and 13.1 ± 1.4% of the sampled mass in PM2.5 and PM1, respectively. The mean NO3 concentrations are 89 ± 15 and 32 ± 5 \(\mu\)g/m\(^3\) in PM2.5 and PM1 samples on January 12, 2013, respectively. NO3 is generally produced by the oxidation of NO2, whose conversion to NO3 also depends on the concentrations of precursor gases and oxidants and on the meteorological conditions. To infer the degree of atmospheric transformation of NO2 to NO3, the nitrogen oxidation ratio (NOR) was calculated. The NOR is defined as follows: \(\text{NOR} = (n-\text{NO3})/(n-\text{NO2}) + (n-\text{NO3})\). The NOR values are 0.16 ± 0.05 and 0.10 ± 0.01 in PM2.5 and PM1, respectively. The concentration of NO2 was very high but the O3 concentration was less than 5.9 \(\mu\)g/m\(^3\) during E1. These results suggested that the photochemical activity was very weak during E1. It has been reported that nitrate is formed via the heterogeneous hydrolysis of N2O5 on the surface of moist PM, especially during humid and hazy weather (Pathak et al., 2009). No matter how complicated the conversion process, NO3 is closely related with high emission of NOx from traffic. Notably, the mean NO3 concentration in PM2.5 is higher than that in PM1. Similar results have been found in European cities (Perrone et al., 2011) and are due to the association of NOx with cations such as Ca\(^{2+}\) and not with NH4\(^+\). The thermal instability of ammonium nitrate, which is only favored under low ambient temperature and high RH, led to the lower particulate nitrate in PM1. Fig. 12 indicates that PM was acidic, which is potentially important in assessing the health effects of airborne particles. Moreover, the acidity of PM2.5 is stronger than that of PM1. The ratio of NO3/SO4\(^{2-}\), which can be used to indicate the relative importance of stationary vs. mobile sources (Sun et al., 2013), indicates that stationary emissions still have a significant effect on PM2.5 pollution. This is in accordance with the high energy consumption and waste gas emission in northern China (Table S1 shows the energy consumption and waste gas emission in Beijing, Tianjin and Hebei province in 2012).

To understand the mechanism of formation of air pollution, the ratio of PM1/PM2.5 and the relationship between the PM1 and PM2.5 mass concentrations are analyzed. As shown in Fig. 13a, the results revealed that the coefficients of determination (\(R^2\)) were 0.85 during E1. The relatively high coefficients imply that PM1 and PM2.5 have similar sources and that they were being influenced by the same meteorological conditions (Charron and Harrison, 2005). E1 is characterized by the low ratio of PM1/PM2.5, 0.44. This result suggests that the peak mass concentrations exist in PM1–2.5. Previous studies (Li et al., 2014) have shown that the presence of organic matter (OM) accelerates the deliquescence of secondary inorganic particles, thereby degrading visibility. With the deliquescence of the particle, liquid layers formed on particle surfaces, which is conducive to the uptake of SO2 and NO2 or of volatile organic compounds. The hygroscopic characteristics led to further growth in the size of PM. In particular, high RH and poor diffusion conditions are conductive to the increase in the size of high concentrations of hygroscopic particles (secondary particles). During E1, OC and water-soluble inorganic ions comprise a large part of PM1 and PM2.5 and thus play an important role in the size of PM. It has been reported that the motion rate of PM1–2.5 is slow, which reduces the probability of collision but increases the probability of deposition (He et al., 2011). Although the movement of PM1–2.5 was slow, the existence of abundant particles (Wang et al., 2013), still has a high probability of collision during E1, which might lead to the existence of the peak mass concentrations in PM1–2.5, not in PM1. Therefore, further studying the formation processes of PM1–2.5 under the stagnant meteorological condition would be helpful to effectively control PM2.5.

E2 is characterized by the high ratio of PM1/PM2.5, 0.70 (Fig. 13b). This is because finer particles can only be transported long distances by wind and other meteorological processes. As shown in Fig. 10, SO4\(^{2-}\), NO3, NH4, OM (OM = 1.4 × OC, Turpin and Lim, 2001) and EC contributed 85.0 ± 20.7% of the measured PM2.5 concentrations in urban areas during E2. SO4\(^{2-}\), NO3 and NH4 accounted for 50.7 ± 18.8% of the PM2.5 mass, and total carbon (EC and OC) accounted for 34.3 ± 7.4% of the PM2.5. SO4\(^{2-}\) contributes, on average, 66.2 ± 38.8 and 43.9 ± 31.7 \(\mu\)g/m\(^3\) to PM2.5 and PM1 samples during E2, respectively. The peak sulfate concentrations occurred at approximately 11:00 on January 27 and 28, 2013. The occurrence of the peak sulfate concentrations is closely related to vertical mixing with the evolution of PBL. It suggested that regional transport led to the results. This increase in the concentrations of sulfate was accompanied by that of nitrate. The nitrate concentrations in PM1 were higher than those in PM1–2.5 during E2. There is obvious evidence that heterogeneous hydrolysis N2O5 on the moist surface of the preexisting PM was responsible for the formation of the high nitrate concentrations in PM2.5 even in the ammonium-poor system. Nitrate is formed on the preexisting sulfate particles, which could provide sufficient surface area, water content of PM, and PM acidity for the hydrolysis of N2O5. In addition, the coupled system of NH4–NO3–SO4\(^{2-}\), in the presence of more secondary organic particles at the aged air masses caused by regional transport, complicates the formation of equilibrium of inorganic particles. Thus, it is particularly critical to understand the formation of inorganic ions and the roles of precursor emissions to achieve compliance in Beijing. The decrease in the NO3/SO4\(^{2-}\) ratio indicates
that the contribution of mobile emission became less significant than that over E1. It is noted that there are almost no peak concentrations of sulfate, nitrate, SO$_2$ and NO$_2$ from local contribution from the night on January 27 to the morning on January 28, 2013. This result is closely related to the decline in SO$_2$ and NO$_2$ emissions on the weekend. However, high regional background sulfate and nitrate were still observed. Therefore, an important implication on PM control strategy is understood in that priorities should be taken to control the emissions of precursors in Beijing as well as surrounding regions. What needs to be stressed is that these acidic gases (SO$_2$ and NO$_2$) in the haze layer could significantly influence atmospheric chemistry downwind.

Another significantly enhanced group of PM was OC and EC. OC and EC in PM$_{2.5}$ averaged 97.2 ± 44.5 and 13.1 ± 6.2 μg m$^{-3}$ on January 29 and were enhanced approximately 315% compared to the values on January 24. The OC/EC ratio exceeding 1.8—2.75 indicating significant presence of SO$_2$ has been reported by Gelencser (2004). The average OC/EC ratio, 7.1 ± 0.5, indicated that an expected result of more SOC formed as well as the deposition of EC during the transport.

4. Conclusions

A number of insights into the characteristics of air pollution and causes of the heaviest particulate air pollution are presented in northern China in this paper. Within the scope of this study, the following conclusions can be drawn:

- The daily average PM$_{2.5}$ concentrations in the study areas during the episodes far exceeded the ambient air quality standards of China and the WHO and even attained the hazardous levels. The increase in anthropogenic emission accompanying the increasing frequency of unfavorable meteorological situations resulted in further degradation of air quality. This result demonstrates that the Chinese government should take immediate action to address regional air pollution and bring a long-term improvement—as a first step, by adjusting the energy supply structure, installing desulfurization and denitrification systems in power plants, stepping up the control of emissions from industrial sources and further tightening motor vehicle emissions and fuel standards.

- The secondary formation of PM was one important mechanism in the formation of heavy pollution episodes. The coupled system of NH$_4$—NO$_3$—SO$_4^{2-}$ is an important contributor to high PM pollution episodes in the presence of high OC concentrations. Special attention should be paid to controlling OC emissions and SOC formation. It is noted that PM$_2.5$ were acidic during the episodes, which is important in assessing the health effects of airborne particles.

This study will enhance our understanding of the mechanism of particular high PM$_{2.5}$ issues. It is evident that more strict control measures should be issued and executed to improve air quality in northern China, in joint development with the authorities of the Beijing—Tianjin—Hebei province. Further work is necessary to quantitatively model source—receptor relationships in the atmospheric environment in northern China.

Acknowledgments

This work was supported by the Key Project of the Chinese Academy of Sciences (XDB05020200). The authors gratefully acknowledge the NOAA Air Resources Laboratory (ARL) for the provision of the HYSPLIT transport and dispersion model and/or READY website (http://www.arl.noaa.gov/ready.php) used in this publication.

Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.atmosenv.2014.04.048.

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