The variation characteristics and possible sources of atmospheric water-soluble ions in Beijing

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Abstract: The North China plain (NCP) including Beijing is currently suffering from severe haze events due to high pollution level of $PM_{2.5}$. To mitigate the serious pollution status, identification of the sources of $PM_{2.5}$ is urgently needed for the effective control measures. Daily samples of $PM_{2.5}$ were collected in Beijing city as well as a rural area in Baoding, Hebei Province through the year of 2014, and the seasonal variation characteristics of water-soluble ions (WSIs) in the $PM_{2.5}$ were comprehensively analyzed for recognizing their possible sources. The results indicated that the periodic emissions from farmers' activities made evident contribution to the atmospheric WSIs in Beijing. The relatively high concentration of K^+ in winter and autumn at the two sampling sites confirmed that crop straw burning made evident contribution to atmospheric K^+ in Beijing. The remarkable elevation of Cl^- at the two sampling sites as well as the evident increase of the Cl^-/K^+ ratio and the Cl^- proportion in WSIs during the winter in Beijing were reasonably ascribed to coal combustion for heating by farmers. The unusually high ratio of Cl^- to Na^+ in summer, the obviously high concentrations of Cl^- in the rural sampling site and the elevation of Cl^- proportion in WSIs in Beijing during the maize fertilization could be rationally explained by the use of the prevailing fertilizer of NH_4Cl in the vast area of NCP. The abnormally high concentrations of Ca^{2+} at the two sampling sites and the elevation of Ca^{2+} proportion during the period of the maize harvest and soil ploughing in Beijing provided convincing evidences that the intensive agricultural activities in autumn made evident contribution to the regional mineral dust. The most serious pollution episodes in autumn were coincident with significant elevation of Ca^{2+}, indicating that the mineral dust emission from the harvest and soil ploughing not only increased the atmospheric concentrations of the primary pollutants, but also greatly accelerated formation of sulfate and nitrate through heterogeneous reactions of NO_2 and SO_2 on the mineral dust. The backward trajectories also indicated that the highest concentrations of WSIs usually occurred in the air parcel from southwest/south regions with high density of farmers. In addition, the values of nitrogen oxidation ratio (NOR) and the sulfur oxidation ratio (SOR) were found to be much higher under haze days than under non-haze days, implying that formation of sulfate and nitrate was greatly accelerated through heterogeneous or multiphase reactions of NO_2 and SO_2 on $PM_{2.5}$.

1. Introduction

The North China plain (NCP) is frequently suffering from severe haze pollution in recent years (Chan and Yao, 2008;Liang et al., 2016), which has aroused great attention from the general public (Zhang et al., 2014;Guo et al., 2014;Huang et al., 2014a;Yang et al., 2015b;Zhang et al., 2015b;Zheng et al., 2015b;Sun et al., 2006). The severe haze pollution is mainly ascribed to elevation of fine particulate matter with dynamic diameter less than 2.5μm ($PM_{2.5}$) (Huang et al., 2014a). $PM_{2.5}$ can directly reduce atmospheric visibility by scattering or absorbing solar light (Seinfeld and Pandis, 1998;Buseck and Posfai, 1999;Cheng et al., 2006) and is harmful to human health (Finlayson-Pitts and Pitts, 2000;Nel, 2005;Poschl, 2005;Peplow, 2014).

To mitigate the serious pollution status, identification of the sources of $PM_{2.5}$ is urgently needed for the effective control measures. Based on field measurements, positive matrix factorization (PMF) (Yu et al., 2013;Wu et al., 2014;Huang et al., 2014a), principal component analysis (PCA) (Wang et al., 2015) and chemical mass balance (CMB) (Huang et al., 2014a;Guo et al., 2012) have been widely used for identifying the sources of $PM_{2.5}$. However, the results of the source apportionment are still not convincing because there are large uncertainties about the indicators, dominant factors and emission inventories used for the identification. For example, some studies suggested traffic emissions in Beijing contributed about 15~20% to the $PM_{2.5}$ (Yu et al., 2013;Wu et al., 2014), while only 4% of the contribution was also reported (Zhang et al., 2013). Additionally, the current source apportionment can only present gross contribution of each source classification, but there are markedly different emissions from individual sources in the same classification. For example, due to the strict control measures and highly efficient combustion, the emissions of pollutants from power plants and big boilers fueled by coal must be totally different from the residential coal stoves on both the emission intensity and composition of pollutants. Finally, most studies about source

apportionment mainly focused on emissions from traffic, industry, construction and secondary formation, whereas the emissions from farmers' activities in the NCP were almost neglected.

There are about 300,000 km^2 agricultural fields and 0.16 billion farmers in the NCP (Zhang et al., 2011). The farmers' activities in the NCP are very seasonal, e.g., the fertilization events and harvests mainly focus on June-July and October-November and residential coal stoves are prevailingly used for heating in winter. The seasonal activities of farmers in the NCP were suspected to make significant contribution to deteriorate the regional air quality, e.g., the most serious pollution events (or haze days) in the NCP were usually coincident with the three seasonal activities of farmers in recent years (Yang et al., 2015b;Huang et al., 2012;Li et al., 2014;Li et al., 2011;Liu et al., 2013;Sun et al., 2013). The serious pollution events during harvest seasons were widely ascribed to crop straw burning (Huang et al., 2012;Li et al., 2014), but the influence of fertilization events and crop straw returning to fields on the regional air quality during the harvest seasons periods was mostly neglected. Strong ammonia (NH_3) emission from the vast agricultural fields in the NCP has been found during fertilization events just after harvest of winter wheat in June-July (Zhang et al., 2011), which must accelerate atmospheric ammonium formation. Although crop straws burning by stealth is still prevailing, most residual crops are being returned into the agricultural fields under the advocacy of government for protecting the air quality. Because crop leaves absorbed large quantities of atmospheric particles during crop growing season (Bealey et al., 2007; Ji et al., 2013), the abrupt release of the particles by smashing crop straw for returning in the vast area of the NCP must also make striking contribution to atmospheric particles in the region during the seasonal harvest seasons. In winter, the serious pollutant emissions from the chimney of the farmers' coal stoves can be easily imagined by the strong smog. Although residential coal consumption only accounts for small

fraction of the total, e.g., ~11% in Beijing-Tianjin-Hebei area (http://hbdczx.mep.gov.cn/pub/), the emission intensity of pollutants from farmers' coal stove is usually about 1-2 magnitude greater than those from power plants (Xu et al., 2006), and the coal consumption by farmers mainly concentrates on the four months in winter.

In this study, to understand the possible influence of farmers' activities on the regional air quality in the NCP, filter samples of $PM_{2.5}$ were daily collected in Beijing city as well as a rural area in Baoding, Hebei Province for a whole year of 2014, and the seasonal variation characteristics of the water-soluble ions (WSIs) in the $PM_{2.5}$ samples were comprehensively investigated in relation to the farmers' activities. The scientific evidences found in this study will be helpful for future control measures in reducing pollutant emissions from rural areas in the NCP.

2. Materials and methods

2.1. Sampling sites

A sampling site in Beijing city was chosen on a rooftop (about 25m above ground) in the Research Center for Eco-Environmental Sciences (here referred to as RCEES, 40°00′29.85″N, 116°20′29.71″E), which is located between the north fourth-ring road and the north fifth-ring road of Beijing and surrounded by some institutes, campuses, and residential areas (Pang and Mu, 2006). Another sampling site in a rural area was selected on the rooftop of a field station (about 5m above ground) which is located in the agricultural field of Dongbaituo village (here referred to as DBT, 38°39′37.36″N, 115°15′16.05″E), Baoding, Hebei Province. The rural sampling site is far away from industries, traffic and commercial emissions. The distance between the two sampling sites is about 170km and the detailed location of the two sampling sites is presented in Fig. 1.

2.2. Sample collection

105 $PM_{2.5}$ samples at the two sites were both collected on Millipore PTFE filters (90mm) by an artificial
106 intelligence's $PM_{2.5}$ sampler (LaoYing-2034) and the sampling flow rate was set to 100L min^{-1}. The
107 duration of each sampling was 24 hours, started at 3:00 p.m. every day and ended at 3:00 p.m. on
108 the next day. All the samples were put in dedicated filter storage containers (90mm, Millipore) after
109 sampling and preserved in a refrigerator till analysis. For the sampling site of RCEES, a total of 235
110 $PM_{2.5}$ samples were collected from January to November of 2014, in winter (Jan 9- Mar 15), spring
111 (Mar 16- May 31), summer (Jun 1- Jun 30, Aug 9- Aug 21) and autumn (Sep 19- Nov 14). To
112 explore the possible influence of farmers' activities, $PM_{2.5}$ samples at DBT were mainly collected
113 during the periods of periodic farmers' activities: heating season in winter (Jan 9- Feb 25), harvest
114 seasons in summer (Jun 9- Jun 22, Aug 9- Aug 17) and autumn (Sep 19- Oct 18, Oct 28- Nov 14).

115 **2.3. Sample analysis**

116 Each sample filter was extracted ultrasonically with 10mL ultrapure water for half an hour. The
117 solutions were filtered through water micro-porous membrane (pore size, 0.45μm; diameter, 13mm)
118 before analysis and the water-soluble ions (WSIs) in the treated filtrates were analyzed by Ion
119 Chromatography (IC, WAYEE IC6200). Five anions (F^-, $HCOO^-$, Cl^-, NO_3^- and SO_4^{2-}) were
120 separated by using an anion column (IC SI-52 4E, 4mmID*250mm) with the eluent (3.6mmol L^{-1}
121 Na_2CO_3) flow rate of 0.8mL min^{-1} and column temperature of 45 ℃. Five cations (Na^+, NH_4^+, Mg^{2+},
122 Ca^{2+} and K^+) were separated by using a cation column (TSKgelSuperIC-CR, 4.6mmID*15cm) with
123 the eluent (2.2mmol L^{-1} MSA and 1mmol L^{-1} 18-crown-6) flow rate of 0.7mL min^{-1} and column
124 temperature of 40 ℃. The relative standard deviation (RSD) of each ion was less than 0.5% for the
125 reproducibility test. The detection limits (S/N=3) were less than 0.001 mg L^{-1} for the anions and
126 cations. At least three filter blanks were analyzed for 60 filter samples, and the average blank values

were about 0.03mg L^{-1} for Na^+, Ca^{2+}, F^-, NO_3^- and SO_4^{2-}, 0.02mg L^{-1} for NH_4^+ and Cl^-, 0.01mg L^{-1} for Mg^{2+}, K^+ and $HCOO^-$. The concentrations of all the ions were corrected for blanks.

2.4. Meteorology, trace gases and back trajectory

The meteorological data, including temperature, wind speed, wind direction, relative humidity (RH), visibility and Air Pollution Index of $PM_{2.5}$, SO_2, NO_2, O_3 at RCEES were from Beijing urban ecosystem research station (http://www.bjurban.rcees.cas.cn/), which is about 20m away from our sampling site of RCEES.

To identify the potential influence of air parcel transport, the air mass backward trajectories were calculated for 72h through the Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT 4) Model of the Air Resources Laboratory of NOAA with NCEP Final analyses data. The backward trajectories arriving at 500m above sampling position were computed at 0:00h, 6:00h, 12:00h and 18:00h (UTC) in each sampling day, respectively. A total of 940 backward trajectories with 72 hourly trajectory endpoints in four seasons were used as input for further analysis.

3. Results and discussion

The ratios of total cation concentration to total anion concentration in different seasons are illustrated in Fig. 2a. The near unity of the ratios indicated excellent charge balance in $PM_{2.5}$ and high quality of the data. The mass concentrations of WSIs and $PM_{2.5}$ at the sampling site of RCEES during the period of Jan 1- Jan 24, 2015 were also simultaneously measured by the filter sampling method and the TEOM 1405 Monitor, respectively. As shown in Fig. 2b, the variation trends of the WSIs and $PM_{2.5}$ were almost the same with a correlation coefficient (R^2) of 0.91, implying that the concentration of WSIs measured could well reveal the pollution status of $PM_{2.5}$. The average mass concentration of WSIs contributed about 80% to the mass of $PM_{2.5}$ measured by the TEOM 1405

149 Monitor, which was much greater than the values of 50-60% reported by previous studies in the
150 NCP (Shen et al., 2009;Li et al., 2013). Therefore, the mass concentration of $PM_{2.5}$ measured by the
151 TEOM 1405 Monitor was suspected to be largely underestimated because the volatile even semi-
152 volatile component in $PM_{2.5}$ can be easily lost at 50 ℃ which is designed in the TEOM 1405 Monitor
153 for avoiding water condensation on the filter (Grover et al., 2005;Liu et al., 2014). It is well
154 documented that temperature is a key factor affecting the distribution of NH_4NO_3 on particle phase
155 due to its thermal decomposition, e.g., at temperature greater than 35 ℃, little NH_4NO_3 is expected
156 under typical ambient conditions (Finlayson-Pitts et al., 1986). The total mass proportions of NO_3^-
157 and NH_4^+ in WSIs usually accounts for about 50% in Beijing city (Yang et al., 2015a), whereas they
158 were found to only account for about 20% in the filters of the TEOM 1405 Monitor, confirming the
159 serious loss of NH_4NO_3 under the high temperature adopted by the TEOM 1405 Monitor.

160 **3.1. Daily variations of WSIs in Beijing city**

161 The daily variations of WSIs at RCEES in each season are illustrated in Fig. 3 and the statistic mass
162 concentrations of the WSIs at RCEES are summarized in Table 1. It is evident that the daily
163 variations of the WSIs at RCEES exhibited significantly periodic fluctuation, indicating
164 meteorological conditions played a pivotal role in accumulation and dissipation of atmospheric
165 pollutants. For example, the most frequently high pollution levels of the WSIs in winter were mainly
166 ascribed to the relatively stable meteorological conditions with the low height of boundary layer
167 which favors pollutants accumulation (Wang et al., 2013;Quan et al., 2014;Tian et al., 2014;Wang
168 et al., 2014;Zhang et al., 2015a). Besides meteorological conditions, the extremely high levels of
169 the WSIs during the pollution episodes revealed strong sources of the pollutants around Beijing.
170 The mean concentrations ($\mu g\ m^{-3}$) of WSIs at RCEES in spring, summer, autumn and winter were

50.5 ± 37.3, 44.2 ± 28.9, 78.3 ± 92.6, and 78.7 ± 61.2, respectively. NO_3^-, SO_4^{2-} and NH_4^+ were found to be the principal ions, accounted for about 80% to the total WSIs in each season, which were in line with previous studies (Hu et al., 2014;Yang et al., 2015a;Huang et al., 2016;Yang et al., 2015b). The three principal ions were mainly ascribed to secondary formation as discussed in the following section. Although the most intensive photochemical reactivity in summer favors sulfate and nitrate formation, the relatively low SO_2 concentration, the fast thermal decomposition of ammonium nitrate and the frequent scavenging by rain events must greatly counteract the contribution of the secondary formation, resulting in the lowest pollution levels of the WSIs in summer. In comparison with other seasons, the remarkable elevation of atmospheric SO_2 and NO_x (see section 3.2.3) in winter would override the relatively low atmospheric photo-oxidants for their oxidation rates and resulted in the highest mean concentration of WSIs. Although the atmospheric concentrations of SO_2 and NO_x in autumn were much smaller than in winter and in spring (see section 3.2.3), the mean concentration of WSIs in autumn was almost the same as that in winter and nearly twice as those in spring and summer, indicating that special mechanisms dominated the secondary formation of the atmospheric principal ions (see section 3.2.3).

3.2. The possible sources for the WSIs

To explore the possible contribution of the periodic emissions from farmers' activities to the WSIs in Beijing, the seasonal variation characteristics of typical WSIs at the urban and rural sites are comparatively illustrated in Fig. 4. It is evident that the seasonal variation of the typical WSIs at the two sites exhibited the similar trend, indicating the similar regional meteorological conditions. The concentrations of the typical WSIs at DBT were generally higher than those at RCEES during the periods of intensive farmers' activities (heating in winter, fertilization in summer and maize harvest

in autumn). To reveal the air mass transport influence on the WSIs in Beijing, three-day backward trajectories for clusters and the corresponding mass concentrations of WSIs during the four seasons in Beijing were analyzed, and the results are illustrated in Fig. 5. It could be seen that the highest concentrations of the typical WSIs were usually observed in the air parcel from southwest/south regions with high density of population. Considering the large fraction (~30%) of air parcel from the southwest/south regions in each season, the human activities in the southwest/south regions made evident contribution to the atmospheric WSIs in Beijing. Besides the industries, the emissions from the high density of farmers in the southwest/south regions of Beijing was also suspected to make evident contribution to the atmospheric WSIs in Beijing.

3.2.1. The sources of K^+ and Cl^-

Without considering the extremely high concentration of K^+ on 1 February and 16 February (Fig. 4) due to firework for celebrating Spring Festival and Lantern Festival (Jiang et al., 2015;Kong et al., 2015), the concentrations of Cl^- and K^+ were much higher in winter and autumn than in spring and summer at the two sites (Fig. 4). The molar ratio of Cl^- to Na^+ at the two sites measured by this study (Fig. 6) in each season was above 1.30 which was greater than the value of 1.18 in fresh sea-salt particles (Brewer, 1975), indicating sources other than sea-salt dominated atmospheric Cl^-. The pronounced correlation coefficients ($r > 0.6$, $p < 0.01$) between K^+ (the indicator for biomass burning, Gao et al., 2011) and Cl^- in winter and autumn indicated that crop straw burning was a common source for K^+ and Cl^- (Li et al., 2014). However, only crop straw burning couldn't explain the relatively high concentrations of Cl^- in winter (Fig. 4), because the average mass Cl^-/K^+ ratio of 7.1 (except for firework event during the Spring Festival) in winter was about a factor of 2 greater than the value of 3.8 in autumn when straw burning was prevailing in the region. Besides straw burning

and sea-salt, coal combustion (Yu et al., 2013;Wu et al., 2014) and biofuel burning (Christian et al., 2010) have been also recognized as the sources for atmospheric Cl^-. Coal have almost been replaced with natural gas and electricity for heating during the winter before 2013 in Beijing city (http://www.radiotj.com/gnwyw/system/2014/07/22/000485853.shtml). Considering the relatively stable Cl^- emissions from coal combustion of industries and power plants as well as biofuel burning during the whole year, the obviously higher Cl^- concentrations measured in winter than in other seasons (Fig. 4) should be ascribed to the additional coal combustion by farmers because of the large amount of residential coal consumption (about 42,000,000 tons) in Beijing-Tianjin-Hebei region and extremely high emission factors of Cl^- (80-300mg Cl^-/kg coal) from the coal combustion (Huang et al., 2014b). The obviously higher Cl^- proportion in winter than in early spring (Fig. 7) provided further evidence for the above conclusion, because the proportion largely counteracted the influence of meteorological factors.

It is interesting to be noted that the remarkably higher Cl^-/Na^+ ratio was observed in summer than in other seasons at RCEES (Fig. 6), which couldn't be explained by the Cl^- sources mentioned above. Fertilization events in the vast agricultural fields of the NCP were suspected to make contribution to atmospheric Cl^- in Beijing because volatile NH_4Cl fertilizer are prevailingly used as the basal fertilization for maize in summer. Based on yearbook of China fertilizer industry (2012), national production of NH_4Cl fertilizers was about 1,174,000 tons in 2011, which was mainly used as the basal fertilization for maize in summer. The obviously high concentrations of Cl^- at DBT (Fig. 4) were indeed observed during the basal fertilization period for maize in June. Compared with the periods before and after maize fertilization, the proportion of Cl^- during maize fertilization in summer increased about 3%-4% (Fig. 7), confirming the influence of maize fertilization on

atmospheric Cl^- in Beijing. The extremely high concentration (about 2ppbv) of Nitryl chloride ($ClNO_2$) observed by Tham et al., 2016 at the same rural site in June indirectly indicated the high concentrations of Cl^- during the period of basal fertilization for maize. Because fertilization is an important source for atmospheric NH_3, the elevation of Cl^- (as a tracer for fertilization) revealed that fertilization in the rural areas around Beijing could also make obvious contribution to atmospheric NH_4^+ in Beijing.

3.2.2. The sources of Ca^{2+}

The remarkably high concentrations of Ca^{2+} occurred in both spring and autumn at RCEES (Fig. 3 and Fig. 4), which were in good agreement with previous studies (Fig. 8). The evident elevation of Ca^{2+} concentrations in spring has been usually ascribed to the frequent dust storm (Zhao et al., 2013b), but there was still no explanation about the extremely high Ca^{2+} concentrations in autumn (Zhao et al., 2013b;Zhang et al., 2013). The intensive maize harvest and soil ploughing in autumn in the vast agricultural fields of the NCP were suspected to make contribution to atmospheric Ca^{2+} in Beijing. Because abundant atmospheric mineral particles were absorbed by crop leaves (Bealey et al., 2007; Ji et al., 2013) during crop growing season, especially in the North China where atmospheric mineral dust is always at high level (Zhang et al., 2013;Zhao et al., 2013b), a large fraction of the mineral dust absorbed on the leaves of crop could be released into the atmosphere during harvest with crop straw being crushed into pieces for returning to fields which is a prevailing cultivation manner under the advocacy of governments for reducing the influence of crop straw burning on the air quality. Additionally, the soil ploughing can also cause the suspension of particles (Fang et al., 2006; Chen et al., 2015). The remarkably high concentrations of Ca^{2+} during the autumn at DBT (Fig. 4) should be ascribed to the above agricultural activities because there are few

construction activities in the rural area. Compared with the periods before and after maize harvest and soil ploughing, the proportion of Ca^{2+} during maize harvest and soil ploughing in autumn increased about 5%-7% (Fig. 7), confirming the influence of maize harvest and soil ploughing on atmospheric Ca^{2+} in Beijing. The back trajectory cluster analysis also supported the above conclusion: the extremely high concentrations of Ca^{2+} in Beijing occurred during the period of 6-25 October (Fig. 3 and Fig. 4) when the air parcels were mainly from the southwest/south regions (Fig. 5) where the vast areas of agricultural field were being under intensive maize harvest and soil ploughing; although the concentrations of Ca^{2+} in the rural area were still kept high levels during the period of 2-14 November (Fig.3 and Fig. 4), the relatively low concentrations of Ca^{2+} in Beijing were observed during the period when the air parcels were mainly from the northwest region (Fig. 5) where agricultural activities are relatively sparse.

3.2.3. The sources of NH_4^+, SO_4^{2-} and NO_3^-

The remarkably high concentrations of NH_4^+, SO_4^{2-} and NO_3^- also appeared in both winter and autumn at the two sites (Fig. 4). NH_4^+ was mainly from the reactions of NH_3 with acid gases (such as HNO_3) and acid particles, and hence its variation trend was the same as those of SO_4^{2-} and NO_3^-. Although atmospheric NH_3 has long been considered to be mainly from agricultural activities, their emissions mainly concentrate on warmer seasons (Krupa, 2003), which cannot explain the frequently high concentrations of NH_4^+ observed in winter. Besides the slow thermal decomposition of ammonium nitrate, strong NH_3 emission sources other than agricultural activities were suspected to be responsible for the frequently high concentrations of NH_4^+ in the cold winter. Besides NH_3 emission from vehicles (Liu et al., 2014), strong emission of NH_3 from residential coal stoves (the NH_3 emission factor was 0.62-1.10g/kg coal) was indeed found by our preliminary measurements,

which was in line with the latest study (Li et al., 2016). During the serious pollution episodes, the concentrations of SO_2 at RCEES in autumn were almost the same as those in summer and about one magnitude lower than in winter (Fig. 9), but the peak concentrations of SO_4^{2-} in autumn were about a factor of 2 greater than those in summer and at almost the same level as those in winter. The gaseous phase reaction with OH (Zhao et al., 2013c;Quan et al., 2014), the heterogeneous reaction on mineral dust (He et al., 2014;Nie et al., 2014), and multiphase reactions in the water of particulate matters (Zheng et al., 2015a) of SO_2 have been recognized to be responsible for atmospheric SO_4^{2-} formation. The significant elevation of both Ca^{2+} and SO_4^{2-} in autumn implied that the heterogeneous reaction of SO_2 on the mineral dust might greatly accelerate the conversion of SO_2 to SO_4^{2-}. Although evidently high concentrations of Ca^{2+} occurred (Fig. 3 and Fig. 4) in spring and SO_2 concentrations were much greater in spring than in autumn (Fig. 9), the SO_4^{2-} concentrations were about a factor of 2 less in spring than in autumn. Atmospheric humidity was suspected to play an important role in the heterogeneous reaction, e.g., the relative humidity was much higher in autumn than in spring during the serious pollution events (Fig. 9). Similar to SO_4^{2-}, the relatively high concentrations of NO_3^- during the serious pollution events in autumn were also ascribed to the heterogeneous reaction of NO_2 on the mineral dust. Therefore, the emission of mineral dust from maize harvest and soil ploughing in autumn also played important roles in secondary formation of nitrate and sulfate in Beijing.

The nitrogen oxidation ratio NOR = $nNO_3^- / (nNO_3^- + nNO_x)$ (n refers to molar concentration) and the sulfur oxidation ratio SOR = $nSO_4^{2-} / (nSO_4^{2-} + nSO_2)$ have been used to estimate the degree of secondary formation of NO_3^- and SO_4^{2-}, which can counteract the interference of meteorological factors (Chan and Yao, 2008;Yu et al., 2013;Guo et al., 2014;Huang et al., 2014a;Yang et al.,

2015b;Zheng et al., 2015b). The values of NOR and SOR during haze days and non-haze days in four seasons are listed in Table 2. Both the values of NOR and SOR on non-haze days were found to be the highest in summer and the lowest in winter, well reflecting the seasonal variation of photochemical intensity. Although sunlight intensity greatly reduced at ground level during haze days, the values of NOR and SOR were about a factor of 2 greater during haze days than during non-haze days in the four seasons, implying again that the heterogeneous or multiphase reactions of SO_2 and NO_2 on atmospheric particles made significant contribution to atmospheric sulfate and nitrate.

3.2.4. The variation characteristics of NO_3^- and SO_4^{2-} during serious pollution episodes

As shown in Fig. 9, the serious pollution episodes with noticeable elevation of various pollutants usually occurred under slow wind speed (less than 2 m s^{-1}) and high relative humidity. In comparison with their precursors of SO_2 and NO_x, the detailed variation trends of SO_4^{2-} and NO_3^- were different, indicating that the elevation of SO_4^{2-} and NO_3^- was not simply ascribed to the physical process of accumulation. It is interesting to be noted that the increasing rates of SO_4^{2-} during some serious pollution events especially with elevation of Ca^{2+} (such as in spring and autumn) were much slower than those of NO_3^- (Fig. 10), implying that the atmospheric heterogeneous reaction of NO_2 on the mineral dust was faster than that of SO_2. Compared with summer and winter, the relatively high ratios of NO_3^-/SO_4^{2-} in spring and autumn (Fig. 6) also supported the above conclusion.

3.3. Comparison with previous studies

The mean concentrations of the three principal ions and some related indicators in Beijing over the past decade are summarized in Table 3. The seasonal variations of the three principal ions reported were quite different, e.g., Huang et al. (2016) found the maximal mean concentrations of SO_4^{2-} and

325 NH_4^+ in the summer and of NO_3^- in the autumn of 2014, whereas in this study all the maximal mean
326 concentrations of the three principal ions appeared in autumn. The mean concentrations of the three
327 ions in autumn in this study were in good agreement with the values reported by Yang et al. (2015).
328 For the mass concentration ratios of NO_3^-/SO_4^{2-} (denoted as N/S), all the investigations exhibited
329 relatively high values in autumn and spring, further confirming that the heterogeneous reaction of
330 NO_2 on mineral dust favored nitrate formation (as discussed above). For NOR and SOR, all
331 investigations were in good agreement, with the highest values in summer, the lowest in winter and
332 higher values during haze days than during clean days. Compared with the investigations of 2003,
333 the evident increase of both the concentration of NO_3^- and the ratio of N/S in recent years revealed
334 the fast increase of vehicle numbers in the decade made significant contribution to atmospheric
335 nitrate.

336 **4. Conclusions**

337 The conspicuous daily fluctuation of the WSIs in each season confirmed that meteorological factors
338 played an important role in governing the accumulation and dispersion of the pollutants. The
339 extremely high concentrations of the WSIs during the serious pollution episodes indicated there
340 were strong sources of the pollutants in Beijing. Based on the comprehensive analysis of the data of
341 the WSIs, the strongly periodic activities of farmers, such as crop harvest, crop straw burning, and
342 coal combustion for heating, were found to make evident contribution to the atmospheric WSIs in
343 Beijing. To mitigate the currently serious pollution status in the NCP including Beijing, the strong
344 emissions of pollutants from the periodic activities of farmers should be aroused great attention.

345 **Author contribution**

346 **Y. J. Mu** designed the experiments and prepared the manuscript. **P. F. Liu** carried out the

experiments and prepared the manuscript. **C. L. Zhang** carried out the experiments. **C. T. Liu**, **C. Y. Xue**, **C. Ye**, **J. F. Liu** and **Y. Y. Zhang** were involved in part of the work. **H. X. Zhang** provided the meteorological data and trace gases.

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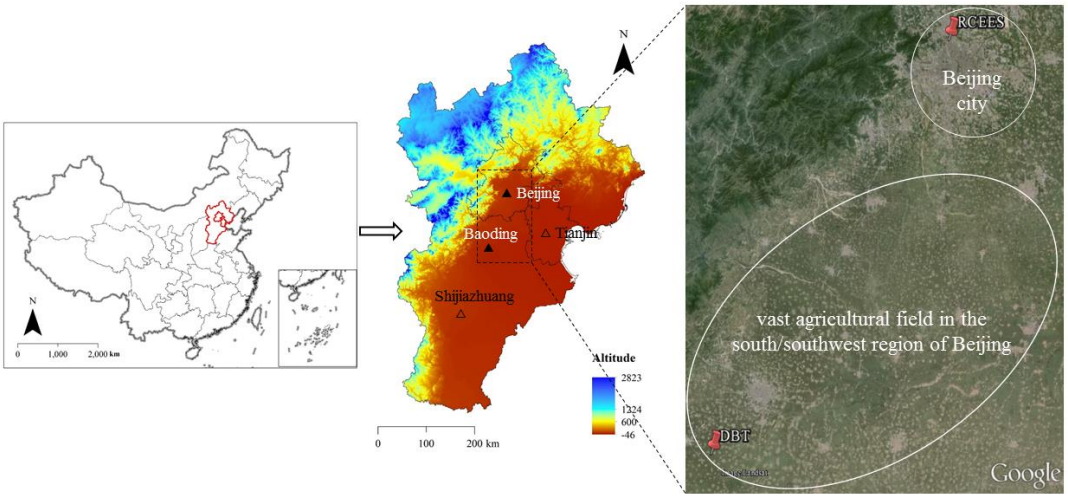


Fig. 1 Sampling sites (the urban site in Beijing city and the rural site in Baoding, Hebei Province) in the NCP.

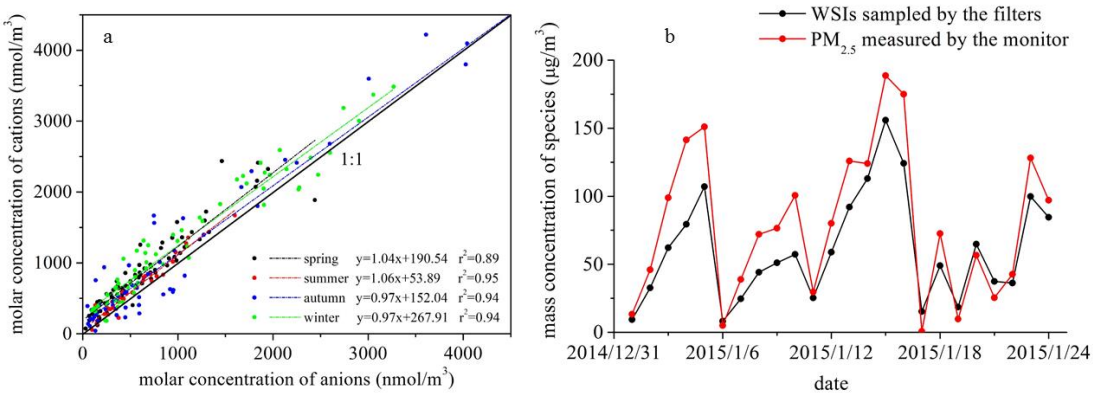
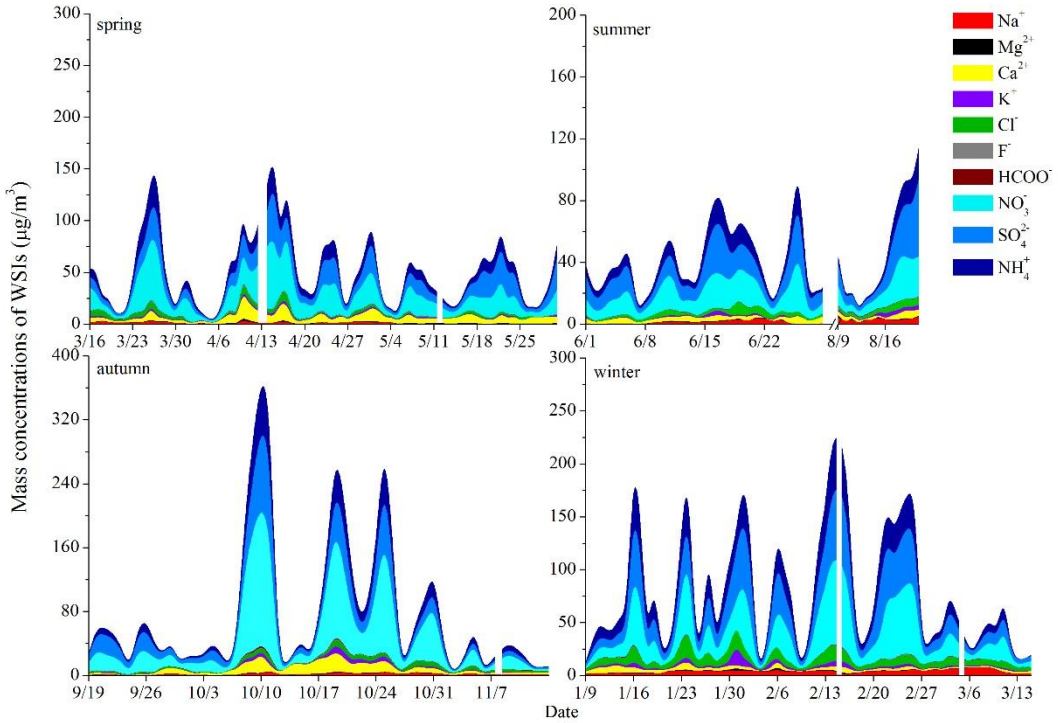


Fig. 2 The ratios of cations to anions in the four seasons of 2014 in Beijing (Fig. 2a), and the comparison between WSIs sampled by the filters and $PM_{2.5}$ measured by the TEOM monitor (Fig. 2b, 1-24 January, 2015).



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571 **Fig. 3** Daily variations of WSIs in each season at RCEES (The smooth lines for the WSIs were drawn between the
572 points of the daily data.).

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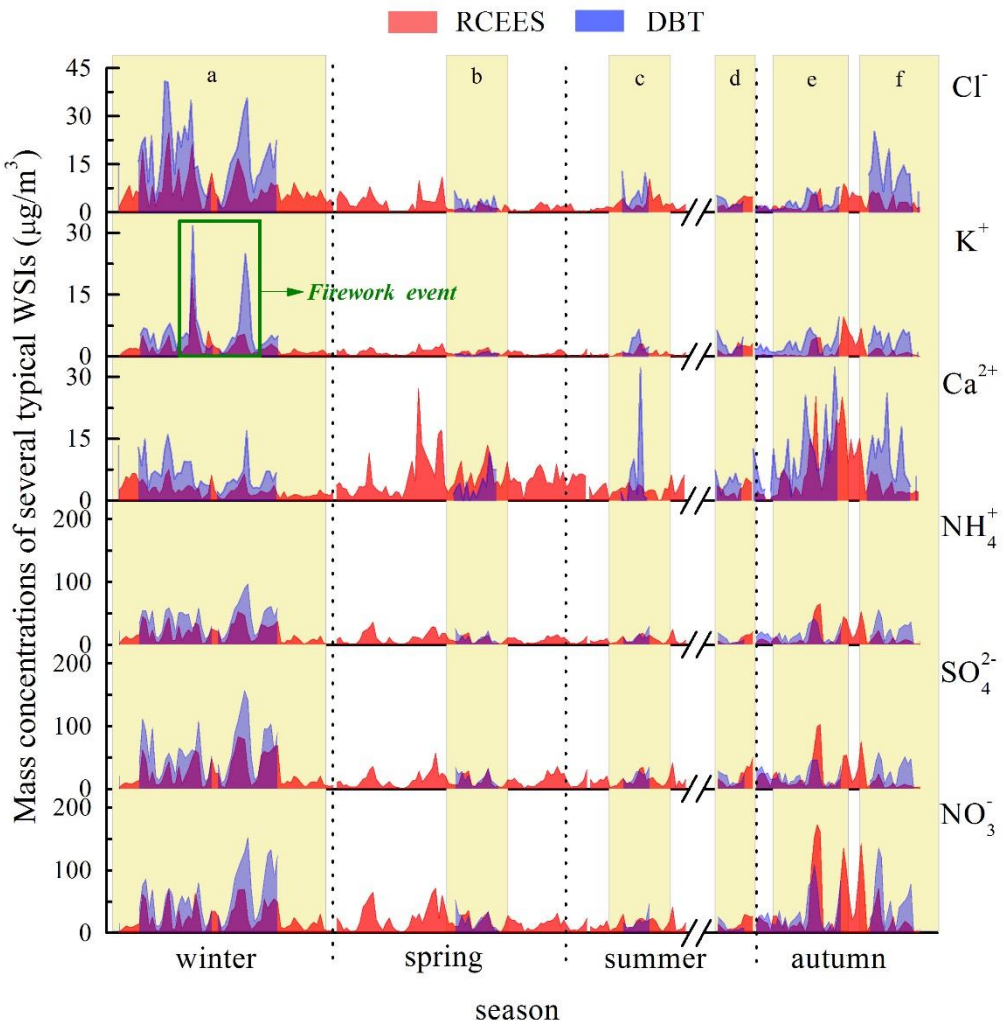

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576 **Fig. 4** Seasonal variations of the several typical WSIs in the year of 2014. (The mass concentrations of Cl^-, K^+,
577 Ca^{2+}, NH_4^+, SO_4^{2-} and NO_3^- were presented at RCEES and DBT. The green square showed the firework event
578 during the period of the Spring Festival. The gray square represented farmers' activities, including residential coal
579 combustion for heating (a), top dressing for wheat (b), wheat harvest and basal fertilization for maize (c), top
580 dressing for maize (d), maize harvest and soil ploughing (e) and straw burning (f).)

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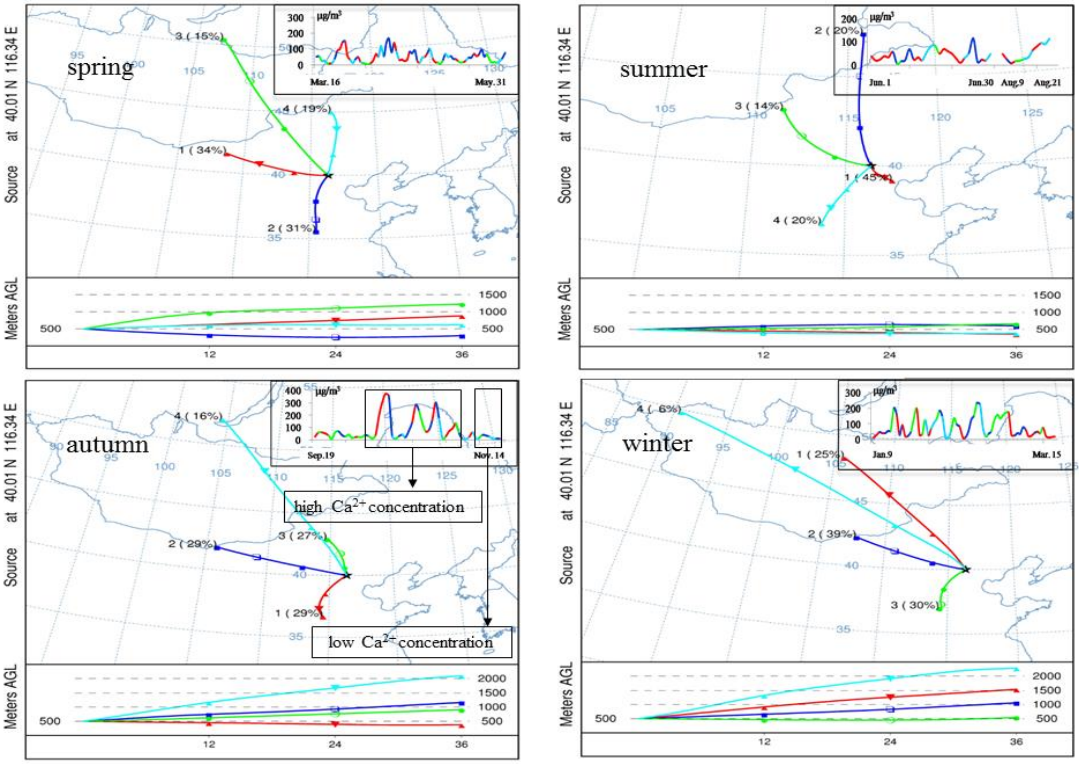

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584 **Fig. 5** The back trajectory cluster analysis and the corresponding overall ion mass concentration during the four
585 seasons in Beijing.
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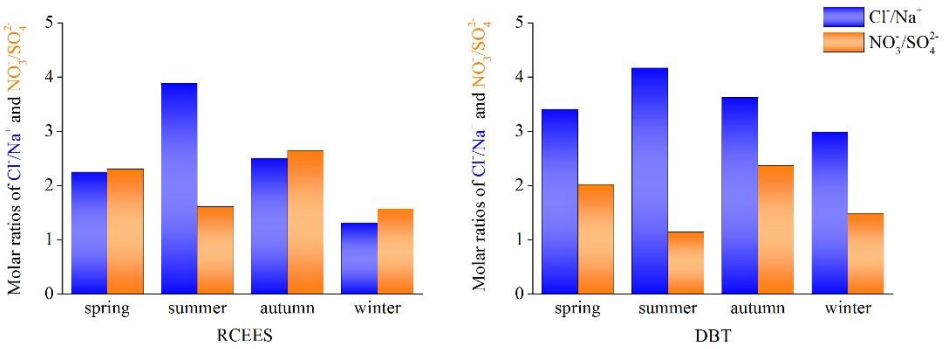

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589 **Fig. 6** The average molar ratios of Cl^-/Na^+ and NO_3^-/SO_4^{2-} in each season at the two sites.
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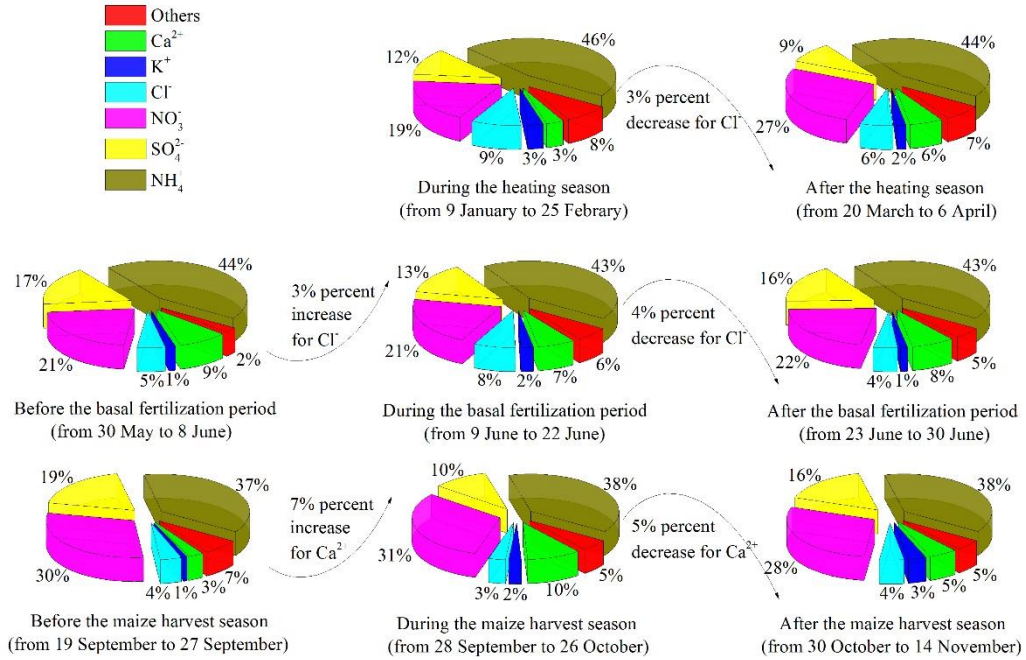

Fig. 7 Molar proportions of atmospheric WSIs at RCEES before, during and after the periods of heating in winter, maize fertilization in summer, and maize harvest and soil ploughing in autumn.

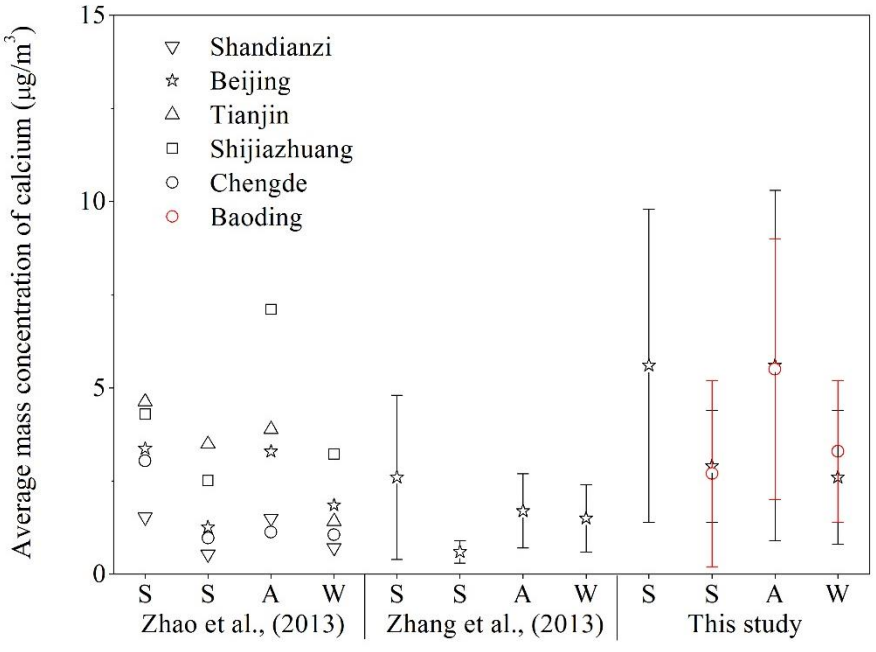

Fig. 8 Comparison of average mass concentration of calcium in four seasons between previous studies and this study for several cities in the NCP (S, S, A and W represent spring, summer, autumn and winter, respectively. The black symbols represent the urban sites and the red symbol represents the rural site (DBT).).

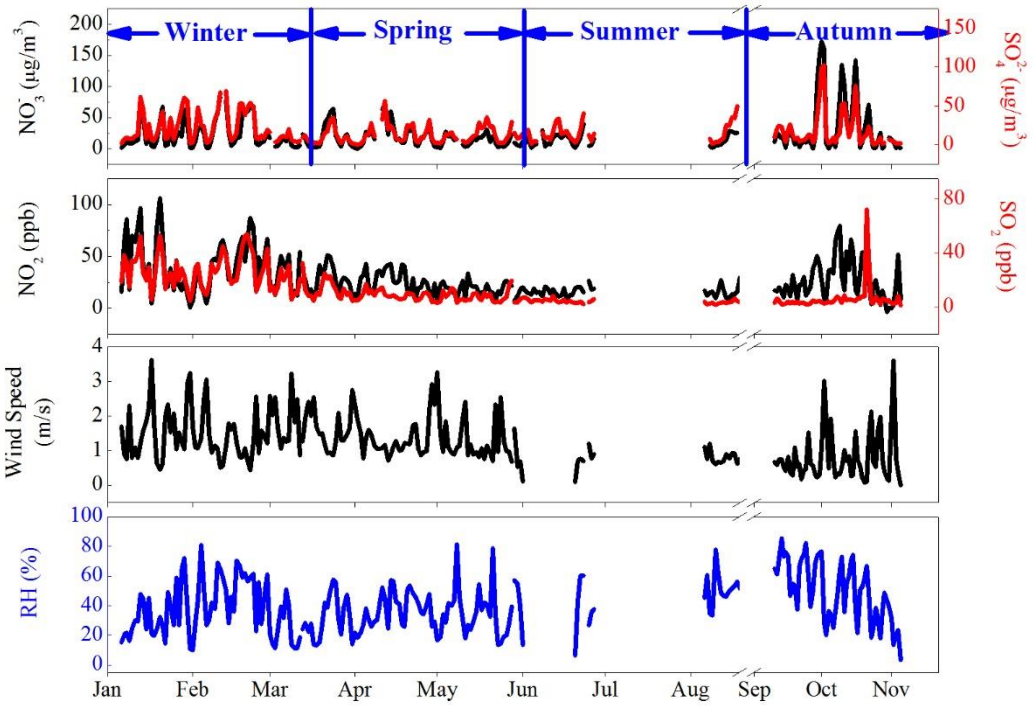

Fig. 9 Time series of NO_3^-, SO_4^{2-}, NO_2 and SO_2 and meteorological data (wind speed and relative humidity) during the four seasons in Beijing for 2014

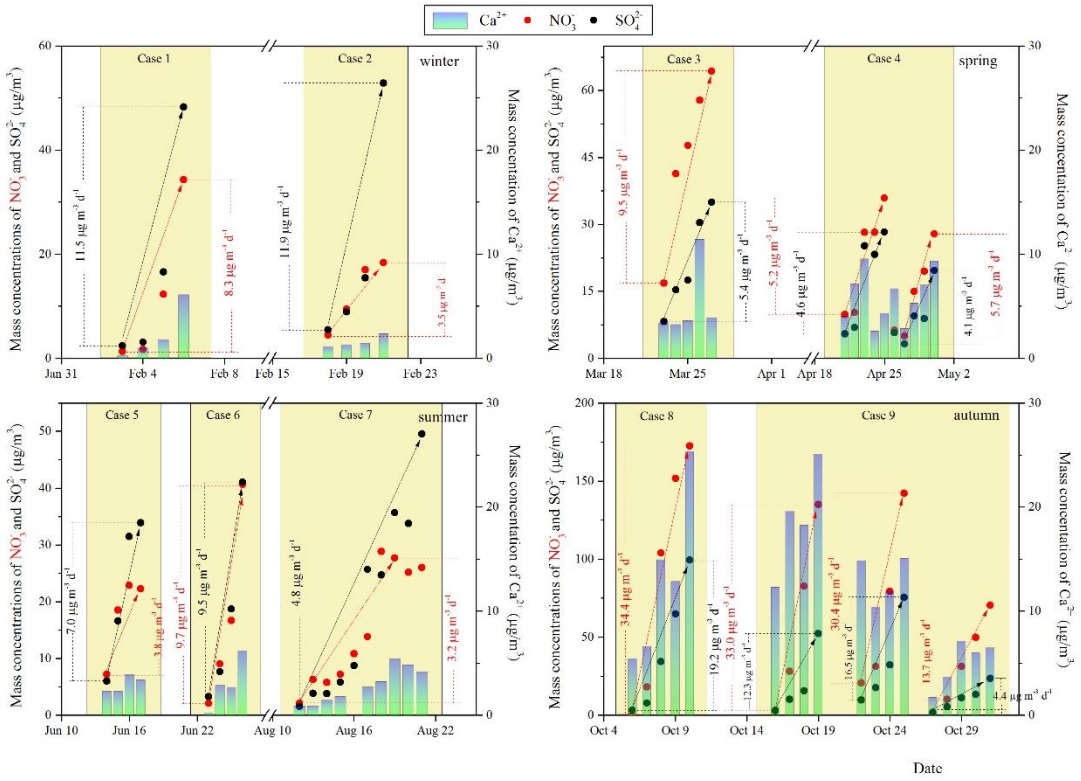

Fig. 10 Case studies about the increasing rates of NO_3^- and SO_4^{2-} with the elevation of Ca^{2+} during serious pollution events in the four seasons.

609 **Table 1** Concentrations (μg m^{-3}) of the WSIs (mean concentrations and standard deviation (SD)) in four seasons at
610 RCEES.

Species	Spring (N=74)		Summer (N=41)		Autumn (N=56)		Winter (N=64)		Annual (N=235)	
	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD
F^-	0.3	0.3	0.2	0.1	0.4	0.2	0.2	0.2	0.3	0.2
$HCOO^-$	0.2	0.1	0.2	0.1	0.4	0.5	0.3	0.2	0.3	0.3
Cl^-	2.4	2.2	2.6	1.9	2.8	2.3	7.0	4.9	3.9	3.7
NO_3^-	18.4	16.0	13.4	9.3	34.3	45.2	23.8	22.8	22.8	27.7
SO_4^{2-}	13.0	10.9	14.6	11.6	18.1	22.8	22.2	19.6	17.0	17.3
Na^+	1.2	0.8	2.1	1.4	1.6	1.1	3.8	1.7	2.3	1.8
NH_4^+	8.8	7.4	7.6	6.0	12.3	16.3	16.5	13.6	11.5	12.2
Mg^{2+}	0.5	0.4	0.3	0.2	0.4	0.3	0.5	0.5	0.4	0.4
Ca^{2+}	5.6	4.2	2.9	1.5	6.8	6.4	2.6	1.8	4.6	4.4
K^+	1.0	0.7	1.1	1.0	1.6	2.2	2.2	2.7	1.5	1.9
Mass	50.5	37.3	44.2	28.9	78.3	92.6	78.7	61.2	63.7	62.0

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613 **Table 2** SOR and NOR during haze days and non-haze days in four seasons at RCEES.

	Spring		Summer		Autumn		Winter	
	SOR	NOR	SOR	NOR	SOR	NOR	SOR	NOR
Haze days	0.3	0.3	0.7	0.4	0.6	0.4	0.2	0.3
Non-haze days	0.2	0.2	0.3	0.2	0.3	0.2	0.1	0.1
Ratio	1.8	1.8	2.0	2.3	2.0	2.6	2.3	2.5

614 The ratio of values in Haze days to that in Non-haze days.

Table 3 Summary of three principal ions (μg m^{-3}), the mass concentration ratio of NO_3^-/SO_4^{2-} (denoted as N/S), NOR and SOR for four seasons at RCEES.

Year	Spring						Summer						Autumn						Winter						Reference
	NO_3^-	SO_4^{2-}	NH_4^+	N/S*	NOR	SOR	NO_3^-	SO_4^{2-}	NH_4^+	N/S	NOR	SOR	NO_3^-	SO_4^{2-}	NH_4^+	N/S	NOR	SOR	NO_3^-	SO_4^{2-}	NH_4^+	N/S	NOR	SOR	
2014	18.4	13.0	8.8	1.4	0.2	0.2	13.4	14.6	7.6	0.9	0.2	0.4	34.3	18.1	12.3	1.9	0.2	0.4	23.8	22.2	16.5	1.1	0.2	0.2	This work
2014(haze)	30.2	21.6	14.5	1.4	0.3	0.3	25.0	28.8	15.3	0.9	0.4	0.7	73.6	36.0	26.5	2.0	0.4	0.6	37.7	34.5	25.4	1.1	0.3	0.2	This work
2014(clean)	7.8	5.2	3.5	1.5	0.2	0.2	8.6	8.7	4.4	1.0	0.2	0.3	8.9	6.5	3.2	1.4	0.2	0.3	5.9	6.4	4.5	0.9	0.1	0.1	This work
2014													35.5	20.0	16.7	1.8	0.2	0.4							Yang et al., 2015b
2013-2014(haze)	14.7	9.0	10.3	1.6	0.2	0.4	33.9	32.7	24.0	1.0	0.3	0.7	40.0	17.4	22.2	2.3	0.2	0.6	22.0	20.4	18.8	1.1	0.2	0.2	Huang et al., 2016
2013-2014(clean)	3.6	2.4	4.4	1.5	0.1	0.2	8.8	8.1	11.7	1.1	0.1	0.4	5.5	4.5	5.6	1.2	0.1	0.4	6.6	5.2	6.0	1.3	0.1	0.1	Huang et al., 2016
2013(haze)	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	26.1	33.3	24.1	0.8	-	-	Tian et al., 2014
2013(clean)	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	4.9	5.0	4.9	1.0	-	-	Tian et al., 2014
2010(haze)	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0.5	0.3	Zhao et al., 2013a
2010(clean)	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0.3	0.2	Zhao et al., 2013a
2009-2010	15.5	14.7	7.5	1.1	-	-	11.8	23.5	11.0	0.5	-	-	10.7	7.9	4.7	1.4	-	-	7.3	8.5	4.5	0.9	-	-	Zhang et al., 2013
2009	-	-	-	-	-	-	12.7	26.1	9.1	0.5	0.2	0.7	6.1	20.1	4.3	0.3	0.1	0.6	-	-	-	-	-	-	Hu et al., 2014
2005	-	-	-	-	-	-	9.9	22.6	4.7	0.4	-	-	-	-	-	-	-	-	-	-	-	-	-	-	Pathak et al., 2009
2001-2003	11.9	13.5	6.5	0.9	0.1	0.1	11.2	18.4	10.1	0.6	0.1	0.4	9.1	12.7	6.3	0.7	0.1	0.2	12.3	21.0	10.6	0.6	0.1	0.1	Wang et al., 2005
2002-2003	-	-	-	-	-	-	12.2	16.0	10.4	0.8	-	-	-	-	-	-	-	-	17.0	30.4	12.9	0.6	-	-	Sun et al., 2004