



The possible contribution of the periodic emissions from farmers' activities in the North China Plain to atmospheric water-soluble ions in Beijing

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Abstract. The North China Plain (NCP), which includes Beijing, is currently suffering from severe haze events due to a high pollution level of PM_{2.5}. To mitigate the serious pollution problem, 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 and in a rural area in Baoding, Hebei Province through the year of 2014, and the seasonal variation of water-soluble ions (WSIs) in PM_{2.5} was comprehensively analysed to determine their possible sources. The results indicated that the periodic emissions from farmers' activities made a significant 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 contributed 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 could be 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 explained by the use of the prevailing fertilizer of NH₄Cl in the vast area of NCP. The abnormally high concentrations of Ca²⁺ at the two sampling sites and the elevation of Ca²⁺ proportion during the period of the maize harvest and soil ploughing

in Beijing provided convincing evidence that the intensive agricultural activities in autumn contributed to the regional mineral dust. The most serious pollution episodes in autumn were coincident with significant elevation of Ca²⁺, 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 NO₂ and SO₂ 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, which have a high density of farmers. In addition, the values of nitrogen oxidation ratio (NOR) and the sulfur oxidation ratio (SOR) were found to be much greater under haze days than under non-haze days, implying that formation of sulfate and nitrate was greatly accelerated through heterogeneous or multiphase reactions of NO₂ and SO₂ 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; R. J. Huang et al., 2014; Y. R. Yang et al., 2015; Y.-L. Zhang

et al., 2015; G. J. Zheng et al., 2015; Sun et al., 2006). The severe haze pollution is mainly ascribed to elevation of fine particulate matter with dynamic diameter less than $2.5\ \mu\text{m}$ ($\text{PM}_{2.5}$) (R. J. Huang et al., 2014). $\text{PM}_{2.5}$ 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; Pöschl, 2005; Peplow, 2014).

To mitigate the serious pollution problem, identification of the sources of $\text{PM}_{2.5}$ is urgently needed for the effective control measures. Based on field measurements, positive matrix factorization (PMF) (Yu et al., 2013; Wu et al., 2014; R. J. Huang et al., 2014), principal component analysis (PCA) (Wang et al., 2015) and chemical mass balance (CMB) (R. J. Huang et al., 2014; Guo et al., 2012) have been widely used for identifying the sources of $\text{PM}_{2.5}$. 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 $\text{PM}_{2.5}$ (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 fuelled by coal must be totally different from the emissions of farmers' coal stoves in 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 often neglected.

There are about $300\,000\ \text{km}^2$ of agricultural fields and 0.16 billion farmers in the NCP (Zhang et al., 2011). The farmers' activities in the NCP are seasonal, e.g. the fertilization events and harvests mainly occur in June–July and October–November and farmers' coal stoves are prevalently 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 (Y. R. Yang et al., 2015; 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 season 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 the wheat harvest (in June–July) (Zhang et al., 2011), which must acceler-

ate atmospheric ammonium formation. Although crop straws burning by stealth is still prevalent, 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 a contribution to atmospheric particles in the region during the seasonal harvest seasons. In winter, heavy smoke from the chimneys of the farmers' coal stoves can be seen everywhere in rural areas of the NCP due to heating supply. Although residential coal consumption only accounts for a small fraction of the total, e.g. $\sim 11\%$ in Beijing–Tianjin–Hebei area (<http://hbdczx.mep.gov.cn/pub/>), the emission factors of typical pollutants such as $\text{PM}_{2.5}$, organic carbon (OC) and polycyclic aromatic hydrocarbons (PAHs) from farmers' coal stoves (about $1054\text{--}12\,910\ \text{mg}\ \text{kg}^{-1}$ for $\text{PM}_{2.5}$, $470\text{--}7820\ \text{mg}\ \text{kg}^{-1}$ for OC and $58.5\text{--}229.1\ \text{mg}\ \text{kg}^{-1}$ for PAHs) are usually about 1–3 orders of magnitude greater than those from coal power plants or industry boilers (about $16\text{--}100\ \text{mg}\ \text{kg}^{-1}$ for $\text{PM}_{2.5}$, $0.3\text{--}17.1\ \text{mg}\ \text{kg}^{-1}$ for OC and $0.8\text{--}12.8\ \mu\text{g}\ \text{kg}^{-1}$ for PAHs) (Zhang et al., 2008; Xu et al., 2006; Geng et al., 2014; Chen et al., 2005; Revuelta et al., 1999; Yang et al., 2016), and the coal consumption by farmers mainly concentrates on the 4 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 $\text{PM}_{2.5}$ were collected daily 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 $\text{PM}_{2.5}$ samples were comprehensively investigated in relation to the farmers' activities. The scientific evidence 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

The sampling site in Beijing city was on a rooftop (about 25 m above ground) in the Research Center for Eco-Environmental Sciences (here referred to as RCEES, $40^\circ 00' 29.85''\ \text{N}$, $116^\circ 20' 29.71''\ \text{E}$), 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 5 m above ground) which is located in the agricultural field of Dongbaituo village (here referred to as DBT, $38^\circ 39' 37.36''\ \text{N}$, $115^\circ 15' 16.05''\ \text{E}$), Baoding, Hebei Province. The rural sampling site is far away from industries, traffic and commercial emissions. The distance between the

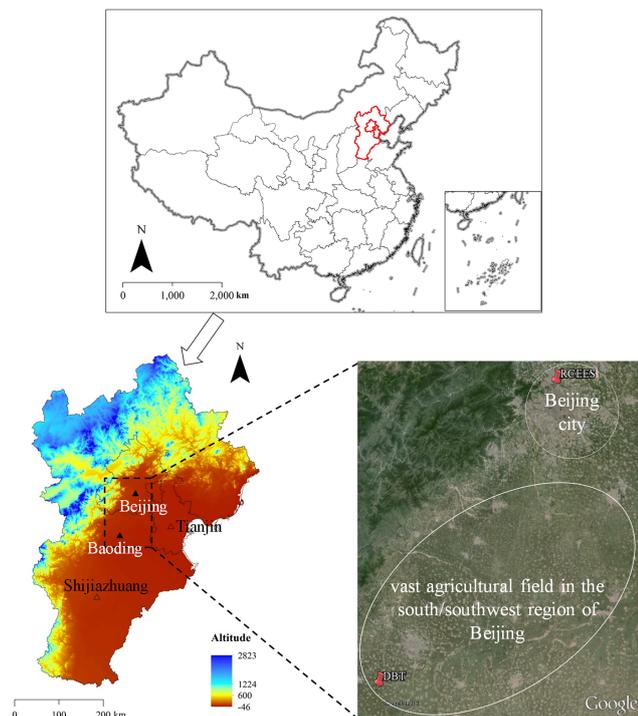


Figure 1. Sampling sites (the urban site in Beijing city and the rural site in Baoding, Hebei Province) in the NCP.

two sampling sites is about 170 km and the detailed location of the two sampling sites is presented in Fig. 1.

2.2 Sample collection

PM_{2.5} samples at the two sites were both collected on Millipore PTFE filters (90 mm) by a PM_{2.5} sampler (LaoYing-2034) and the sampling flow rate was set to 100 L min⁻¹. The duration of each sampling was 24 h, starting at 03:00 p.m. every day and ending at 03:00 p.m. (UTC + 8) on the next day. All the samples were put in dedicated filter storage containers (90 mm, Millipore) after sampling and preserved in a refrigerator till analysis. For the sampling site of RCEES, a total of 235 PM_{2.5} samples were collected from January to November of 2014, in winter (9 January–15 March), spring (16 March–31 May), summer (1–30 June, 9–21 August) and autumn (19 September–14 November). To explore the possible influence of farmers' activities, PM_{2.5} samples at DBT were mainly collected during the periods of periodic farmers' activities: heating season in winter (9 January–25 February), harvest seasons in summer (9–22 June, 9–17 August) and autumn (19 September–18 October, 28 October–14 November).

2.3 Sample analysis

Each sample filter was extracted ultrasonically with 10 mL ultrapure water for half an hour. The solutions were fil-

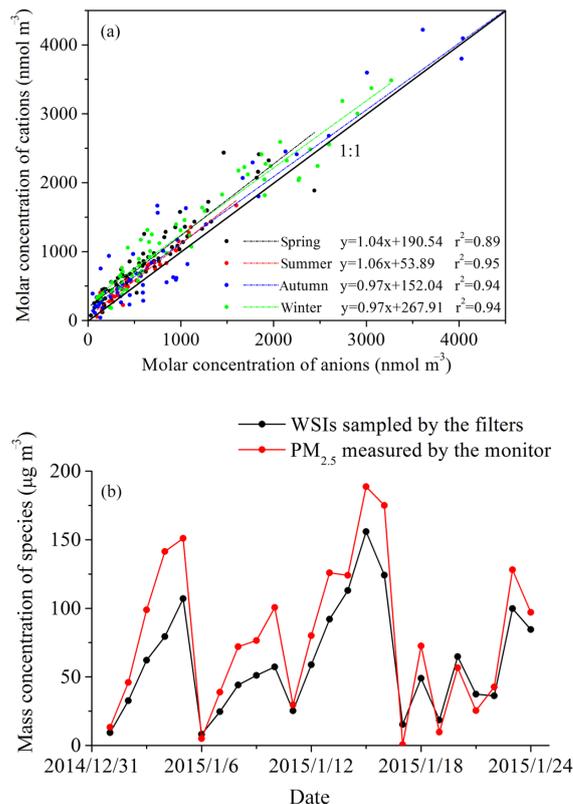


Figure 2. The ratios of cations to anions in the four seasons of 2014 in Beijing (a), and the comparison between WSIs sampled by the filters and PM_{2.5} measured by the TEOM monitor (b, 1–24 January 2015).

tered through a micro-porous membrane (pore size, 0.45 μm; diameter, 13 mm) before analysis and the WSIs in the treated filtrates were analysed by Ion Chromatography (IC, WAYEE IC6200). Five anions (F⁻, HCOO⁻, Cl⁻, NO₃⁻ and SO₄²⁻) were separated by using an anion column (IC SI-52 4E, 4 mmID × 250 mm) with the eluent (3.6 mmol L⁻¹ Na₂CO₃) flow rate of 0.8 mL min⁻¹ and column temperature of 45 °C. Five cations (Na⁺, NH₄⁺, Mg²⁺, Ca²⁺ and K⁺) were separated by using a cation column (TSKgelSuperIC-CR, 4.6 mmID × 15 cm) with the eluent (2.2 mmol L⁻¹ MSA and 1 mmol L⁻¹ 18-crown-6) flow rate of 0.7 mL min⁻¹ and column temperature of 40 °C. The relative standard deviation (RSD) of each ion was less than 0.5 % for the reproducibility test. The detection limits ($S/N = 3$) were less than 0.001 mg L⁻¹ for the anions and cations. At least three filter blanks were analysed for 60 filter samples, and the average blank values were about 0.03 mg L⁻¹ for Na⁺, Ca²⁺, F⁻, NO₃⁻ and SO₄²⁻, 0.02 mg L⁻¹ for NH₄⁺ and Cl⁻, 0.01 mg L⁻¹ for Mg²⁺, K⁺ and HCOO⁻. The concentrations of all the ions were corrected for blanks.

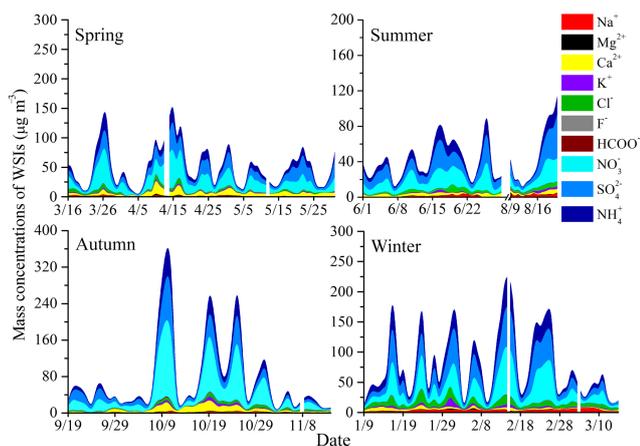


Figure 3. Variation of WSIs in each season at RCEES (the smooth lines for the WSIs were drawn between the points of the daily data.).

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}, SO₂, NO₂, O₃ at RCEES were from Beijing urban ecosystem research station (<http://www.bjurban.rcees.cas.cn/>), which is about 20 m away from our sampling site of RCEES.

To identify the potential influence of air parcel transport, the air mass backward trajectories were calculated for 72 h through the Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPPLIT 4) Model of the Air Resources Laboratory of NOAA with NCEP Final analyses data. The backward trajectories arriving at 500 m above sampling position were computed at 00:00, 06:00, 12:00 and 18:00 (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 (defined as $[Na^+] + [NH_4^+] + 2 \times [Mg^{2+}] + 2 \times [Ca^{2+}] + [K^+]$) to total anion concentration (defined as $[F^-] + [HCOO^-] + [Cl^-] + [NO_3^-] + 2 \times [SO_4^{2-}]$) 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 1–24 January 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 be used as an indicator of the pollution level. The average mass concentration of WSIs contributed about 80 % to the mass of

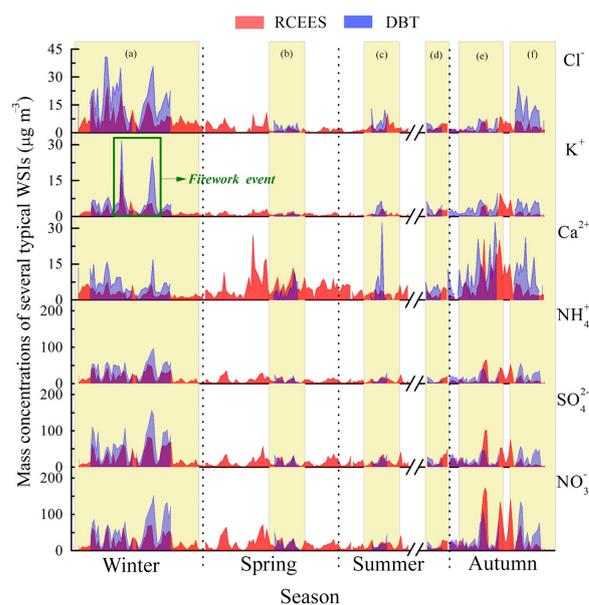


Figure 4. Concentrations of selected WSIs in the year of 2014. (The mass concentrations of Cl⁻, K⁺, Ca²⁺, NH₄⁺, SO₄²⁻ and NO₃⁻ were presented at RCEES and DBT. The green square shows the firework event during the period of the Spring Festival. The areas shaded in yellow represent farmers' activities, including residential coal combustion for heating (a), top dressing for wheat (b), wheat harvest and basal fertilization for maize (c), top dressing for maize (d), maize harvest and soil ploughing (e) and straw burning (f).)

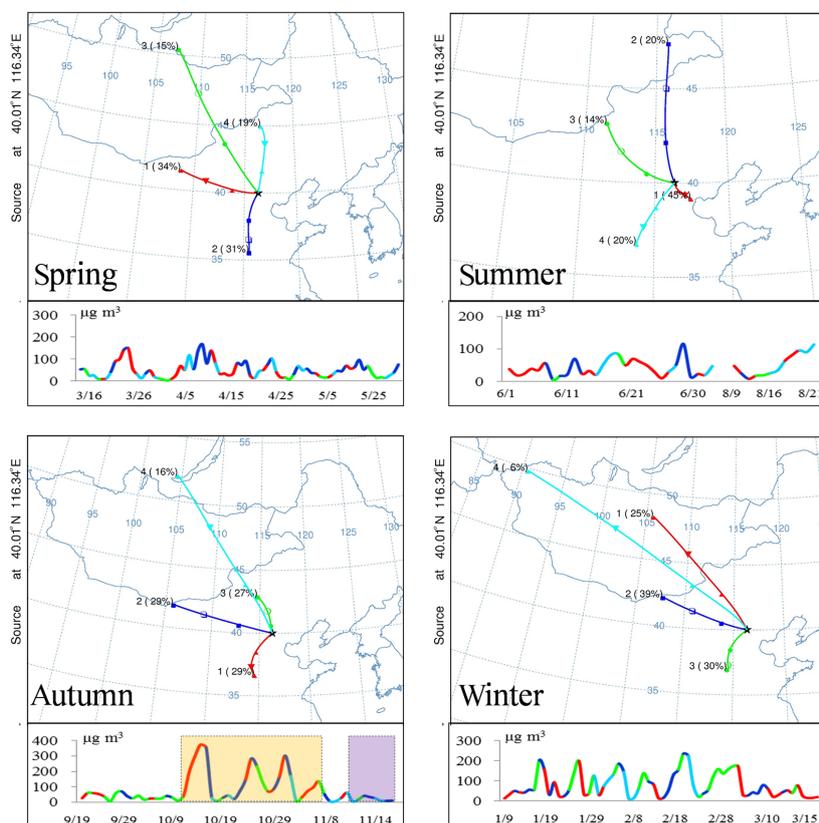
PM_{2.5} measured by the TEOM 1405 Monitor, which was much greater than the values of 50–60 % reported by previous studies in the NCP (Shen et al., 2009; Li et al., 2013). It was possible that the mass concentration of PM_{2.5} measured by the TEOM 1405 Monitor was underestimated because the volatile even semi-volatile component in PM_{2.5} can be easily lost at 50 °C which is designed in the TEOM 1405 Monitor for avoiding water condensation on the filter (Charron et al., 2004; Grover et al., 2005; C. N. Liu et al., 2014). It is well documented that temperature is a key factor affecting the distribution of NH₄NO₃ on particle phase due to its thermal decomposition, e.g. at a temperature greater than 35 °C, little NH₄NO₃ is expected under typical ambient conditions (Finlayson-Pitts and Barbara, 1986). The total mass proportions of NO₃⁻ and NH₄⁺ in WSIs usually account for about 50 % in Beijing city (Y. Yang et al., 2015), whereas they were found to only account for about 20 % in the filters of the TEOM 1405 Monitor in this study, confirming the serious loss of NH₄NO₃ under the high temperature adopted by the TEOM 1405 Monitor.

3.1 Daily variations of WSIs in Beijing city

The daily variation of WSIs at RCEES in each season is illustrated in Fig. 3 and the average mass concentrations of the

Table 1. Concentrations ($\mu\text{g m}^{-3}$) of the WSIs (mean concentrations and standard deviation (SD)) in four seasons at 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

**Figure 5.** The back trajectory cluster analysis and the corresponding overall ion mass concentration during the four seasons in Beijing. (The area shaded in yellow represents the period with the high concentrations of Ca^{2+} both at RCEES and DBT. The area shaded in purple represents the period with the high concentrations of Ca^{2+} at DBT but the low concentrations of Ca^{2+} at RCEES (See Fig. 4).)

WSIs at RCEES are summarized in Table 1. It is evident that the concentration of the WSIs varied greatly on a timescale of days, indicating meteorological conditions played a pivotal role in accumulation and dissipation of atmospheric pollutants. For example, the highest frequency pollution levels of the WSIs in winter were mainly ascribed to the relatively sta-

ble meteorological conditions with the low height of boundary layer which favoured pollutants' accumulation (Wang et al., 2013; Quan et al., 2014; Tian et al., 2014; Wang et al., 2014; L. Zhang et al., 2015). Besides meteorological conditions, the extremely high levels of the WSIs during the pollu-

tion episodes revealed strong sources of the pollutants around Beijing.

The mean concentrations ($\mu\text{g m}^{-3}$) 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% of the total WSIs in each season, which were in line with previous studies (Hu et al., 2014; Y. Yang et al., 2015; Huang et al., 2016; Y. R. Yang et al., 2015). The three principal ions were mainly ascribed to secondary formation as discussed in the following section. Although the most intensive photochemical reactivity in summer favours sulfate and nitrate formation, the relatively low SO_2 concentration, the reduced gas-to-particle partitioning 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 large elevation of atmospheric SO_2 and NO_x (see Sect. 3.2.3) in winter would result in large sulfate and nitrate formation rates despite the lower concentrations of oxidizing species and cause 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 Sect. 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 Sect. 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 concentrations of typical WSIs at the urban and rural sites are compared 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 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, 3-day backward trajectories for clusters and the corresponding mass concentrations of WSIs during the four seasons in Beijing were analysed, 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 parcels from southwest–south regions with high density of population. Considering the large fraction ($\sim 30\%$) of air parcels from the southwest–south regions in each season, the human activities in the southwest–south regions contributed 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 affect the atmospheric WSIs in Beijing.

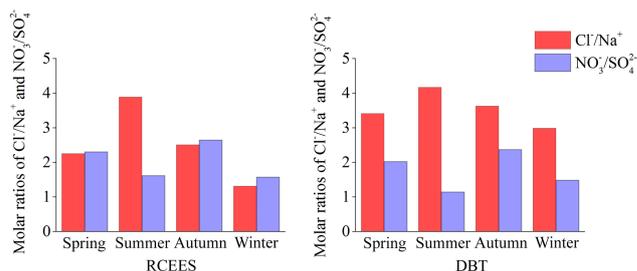


Figure 6. The average molar ratios of $\text{Cl}^- / \text{Na}^+$ and $\text{NO}_3^- / \text{SO}_4^{2-}$ in each season at the two sites.

3.2.1 The sources of K^+ and Cl^-

With the exception of the extremely high concentrations of K^+ on 1 and 16 February (Fig. 4) due to fireworks 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 could not explain the relatively high concentrations of Cl^- in winter (Fig. 4), because the average molar Cl^- / K^+ ratio of 7.8 (except for firework events during the Spring Festival) in winter was about a factor of 2 greater than the value of 4.2 in autumn when straw burning prevailed 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 has almost been replaced with natural gas and electricity for heating during the winter before 2013 in Beijing city (Ma et al., 2015). 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 Tg year^{-1}) in the Beijing–Tianjin–Hebei region and extremely high emission factors of Cl^- ($80\text{--}300 \text{ mg kg}^{-1}$ coal) from the coal combustion (W. Huang et al., 2014). 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.

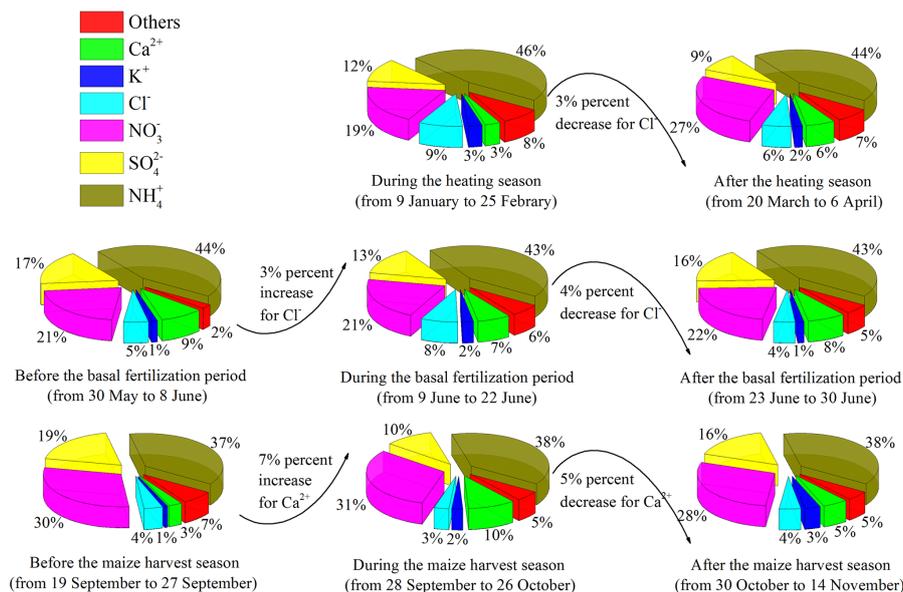


Figure 7. Molar fractions of atmospheric WSIs at RCEES before, during and after the periods of heating in winter, maize fertilization in summer, and maize harvest and soil ploughing in autumn.

It is interesting to note that the remarkably higher Cl^-/Na^+ ratio was observed in summer than in other seasons at RCEES (Fig. 6), which could not be explained by the Cl^- sources mentioned above. Fertilization events in the vast agricultural fields of the NCP were suspected to contribute to atmospheric Cl^- in Beijing because volatile NH_4Cl fertilizer are prevalently used as the basal fertilization for maize in summer. Based on the yearbook of the China fertilizer industry (2012), national production of NH_4Cl fertilizers was about 1.174 Tg 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 2 ppbv) 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 an 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 (Figs. 3 and 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 storms (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 contribute 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 North China where atmospheric mineral dust is always at a 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 method 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 by 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: (1) the extremely high concentrations of Ca^{2+} in Beijing occurred during the period of 6–25 October (Figs. 3 and 4) when the air parcels were mainly from the southwest–south regions (Fig. 5) where the vast areas of agricultural

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

The ratio of values in haze days to that in non-haze days.

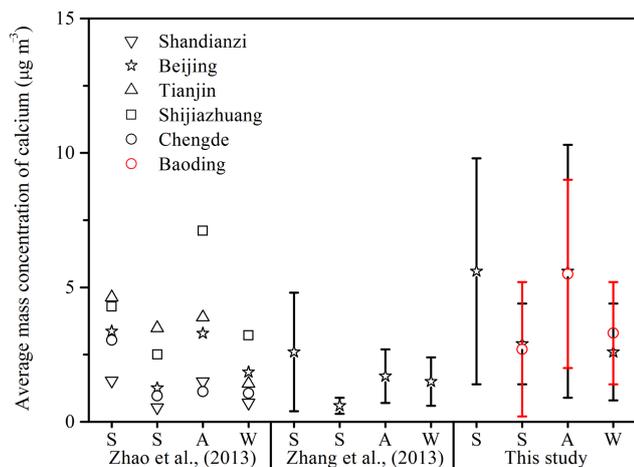


Figure 8. Comparison of average mass concentrations of calcium in four seasons between previous studies and this study for several cities in the NCP (S, S, A and W represent spring, summer, autumn and winter, respectively). The black symbols represent the urban sites and the red symbol represents the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

field were under intensive maize harvest and soil ploughing. (2) Although the concentrations of Ca^{2+} in the rural area remained at high levels during the period of 2–14 November (Figs. 3 and 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^-

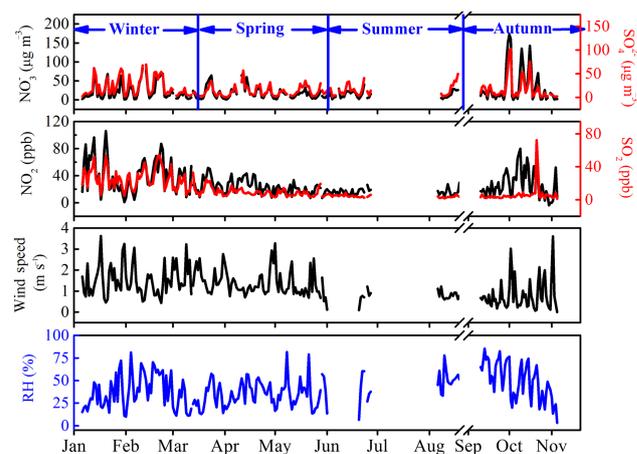
The remarkably high concentrations of NH_4^+ , SO_4^{2-} and NO_3^- also appeared in both winter and autumn at the two sites (Fig. 4). NH_4^+ was mainly from the reactions of NH_3 with acid gases (such as HNO_3) and acid particles, and hence its variation trend was the same as those of SO_4^{2-} and 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 frequent high concentrations of NH_4^+ observed in winter. Besides the increased gas-to-particle partitioning of ammonium nitrate at lower temperatures, strong NH_3 emission sources other than agricultural activities were

suspected to be responsible for the frequent high concentrations of NH_4^+ in the cold winter. Besides NH_3 emission from vehicles (T. Y. Liu et al., 2014), strong emission of NH_3 from farmers' coal stoves (the NH_3 emission factor was $0.62\text{--}1.10\text{ g kg}^{-1}$ 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 1 order of 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., 2013; Quan et al., 2014), the heterogeneous reaction on mineral dust (He et al., 2014; Nie et al., 2014), and multiphase reactions in the aerosol water (B. Zheng et al., 2015) 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 (Figs. 3 and 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 $\text{NOR} = n\text{NO}_3^- / (n\text{NO}_3^- + n\text{NO}_x)$ (n refers to molar concentration) and the sulfur oxidation ratio $\text{SOR} = n\text{SO}_4^{2-} / (n\text{SO}_4^{2-} + n\text{SO}_2)$ 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; R. J. Huang et al., 2014; Y. R. Yang et al., 2015; G. J. Zheng et al., 2015). The values of NOR and SOR during haze days and non-haze days in four seasons are listed

Table 3. Summary of three principal ions ($\mu\text{g m}^{-3}$), the molar concentration ratio of $\text{NO}_3^- / \text{SO}_4^{2-}$ (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	2.2	0.2	0.2	13.4	14.6	7.6	1.4	0.2	0.4	34.3	18.1	12.3	2.9	0.2	0.4	23.8	22.2	16.5	1.7	0.2	0.2	This work	
2014 (haze)	30.2	21.6	14.5	2.2	0.3	0.3	25.0	28.8	15.3	1.4	0.4	0.7	73.6	36.0	26.5	3.1	0.4	0.6	37.7	34.5	25.4	1.7	0.3	0.2	This work	
2014 (clean)	7.8	5.2	3.5	2.3	0.2	0.2	8.6	8.7	4.4	1.5	0.2	0.3	8.9	6.5	3.2	2.2	0.2	0.3	5.9	6.4	4.5	1.4	0.1	0.1	This work	
2014	14.7	9.0	10.3	2.5	0.2	0.4	33.9	32.7	24.0	1.5	0.3	0.7	35.5	20.0	16.7	2.8	0.2	0.4	22.0	20.4	18.8	1.7	0.2	0.2	Y. R. Yang et al. (2015)	
2013–2014 (haze)	3.6	2.4	4.4	2.3	0.1	0.2	8.8	8.1	11.7	1.7	0.1	0.4	40.0	17.4	22.2	3.6	0.2	0.6	6.6	5.2	6.0	2.0	0.1	0.1	Huang et al. (2016)	
2013–2014 (clean)	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	26.1	33.3	24.1	1.2	–	–	Huang et al. (2016)	
2013 (haze)	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	4.9	5.0	4.9	1.5	–	–	Tian et al. (2014)	
2010 (haze)	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	Tian et al. (2014)	
2010 (clean)	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	Zhao et al. (2013a)
2010	15.5	14.7	7.5	1.7	–	–	11.8	23.5	11.0	0.8	–	–	10.7	7.9	4.7	2.2	–	–	7.3	8.5	4.5	1.4	–	–	–	Zhao et al. (2013a)
2009–2010	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	Zhang et al. (2013)
2009	–	–	–	–	–	–	9.9	22.6	4.7	0.6	–	–	6.1	20.1	4.3	0.5	0.1	0.6	–	–	–	–	–	–	–	Hu et al. (2014)
2005	–	–	–	–	–	–	11.2	18.4	10.1	0.9	0.1	0.4	9.1	12.7	6.3	1.1	0.1	0.2	–	–	–	–	–	–	–	Pathak et al. (2009)
2001–2003	11.9	13.5	6.5	1.4	0.1	0.1	12.2	16.0	10.4	1.2	–	–	–	–	–	–	–	–	12.3	21.0	10.6	0.9	0.1	0.1	–	Wang et al. (2005)
2002–2003	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	17.0	30.4	12.9	0.9	–	–	–	Sun et al. (2004)

**Figure 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.

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, 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 a 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 note 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 $\text{NO}_3^- / \text{SO}_4^{2-}$ 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)

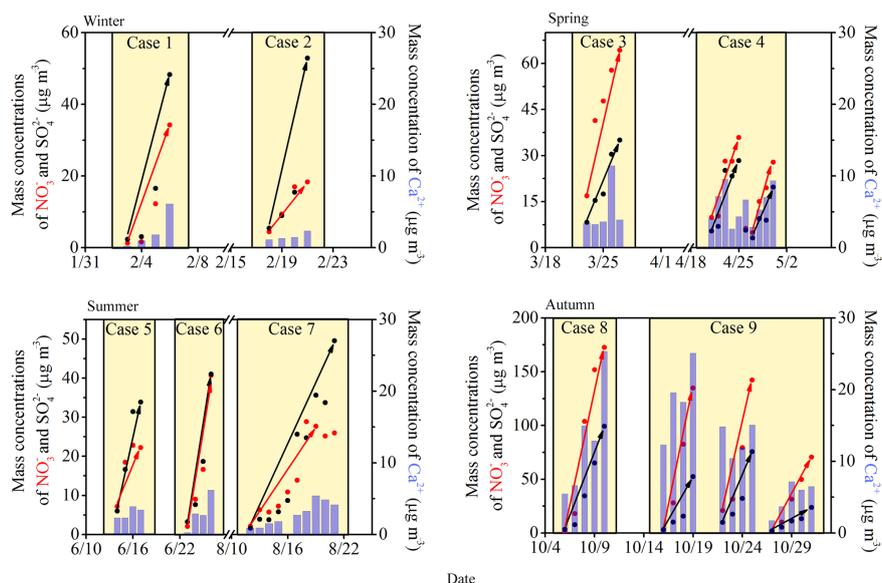


Figure 10. Case studies about the increasing rates of NO_3^- and SO_4^{2-} with the elevation of Ca^{2+} during serious pollution events in the four seasons.

found the maximal mean concentrations of SO_4^{2-} and NH_4^+ in the summer and of NO_3^- in the autumn of 2014, whereas in this study all the maximal mean concentrations of the three principal ions appeared in autumn. The mean concentrations of the three ions in autumn in this study were in good agreement with the values reported by Yang et al. (2015). For the molar concentration ratios of $\text{NO}_3^- / \text{SO}_4^{2-}$ (denoted as N/S), all the investigations exhibited relatively high values in autumn and spring, further confirming that the heterogeneous reaction of NO_2 on mineral dust favoured nitrate formation (as discussed above). For NOR and SOR, all investigations were in good agreement, with the highest values in summer, the lowest in winter and higher values during haze days than during clean days. Compared with the investigations of 2003, the evident increase of both the concentration of NO_3^- and the ratio of N/S in recent years revealed the fast increase of vehicle numbers in the decade made a significant contribution to atmospheric nitrate.

4 Conclusions

The large daily fluctuation of the WSIs in each season confirmed that meteorological factors played an important role in governing the accumulation and dispersion of the pollutants. The extremely high concentrations of the WSIs during the serious pollution episodes indicated there were strong sources of the pollutants in Beijing. Based on the comprehensive analysis of the data of the WSIs, the farmers' activities, such as crop harvest, crop straw burning, and coal combustion for heating, were found to contribute to the atmospheric WSIs in Beijing. To mitigate the currently serious pollution

status in the NCP including Beijing, greater attention should be paid to the strong emissions of pollutants from the periodic activities of farmers.

5 Data availability

All data described here are available upon request from the corresponding author.

Author contributions. 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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