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 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 $PM_{2.5}$ were comprehensively analyzed 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 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 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 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, 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 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 2.5 μm ($PM_{2.5}$) (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 problem, 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 emissions of farmers'

61   coal stoves in both the emission intensity and composition of pollutants. Finally, most studies about

62   source apportionment mainly focused on emissions from traffic, industry, construction and

63   secondary formation, whereas the emissions from farmers' activities in the NCP were often

64   neglected.

65   There are about 300,000 km^2 of agricultural fields and 0.16 billion farmers in the NCP (Zhang et

66   al., 2011). The farmers' activities in the NCP are seasonal, e.g., the fertilization events and harvests

67   mainly occur in June-July and October-November and farmers' coal stoves are prevailingly used for

68   heating in winter. The seasonal activities of farmers in the NCP were suspected to make significant

69   contribution to deteriorate the regional air quality, e.g., the most serious pollution events (or haze

70   days) in the NCP were usually coincident with the three seasonal activities of farmers in recent years

71   (Yang et al., 2015b;Huang et al., 2012;Li et al., 2014;Li et al., 2011;Liu et al., 2013;Sun et al., 2013).

72   The serious pollution events during harvest seasons were widely ascribed to crop straw burning

73   (Huang et al., 2012;Li et al., 2014), but the influence of fertilization events and crop straw returning

74   to fields on the regional air quality during the harvest seasons periods was mostly neglected. Strong

75   ammonia (NH_3) emission from the vast agricultural fields in the NCP has been found during

76   fertilization events just after the wheat harvest (in June-July) (Zhang et al., 2011), which must

77   accelerate atmospheric ammonium formation. Although crop straws burning by stealth is still

78   prevalent, most residual crops are being returned into the agricultural fields under the advocacy of

79   government for protecting the air quality. Because crop leaves absorbed large quantities of

80   atmospheric particles during crop growing season (Bealey et al., 2007; Ji et al., 2013), the abrupt

81   release of the particles by smashing crop straw for returning in the vast area of the NCP must also

82   make a contribution to atmospheric particles in the region during the seasonal harvest seasons. In

83   winter, heavy smoke from the chimneys of the farmers' coal stoves can be seen everywhere in rural

84   areas of the NCP due to heating supply. Although residential coal consumption only accounts for a

85   small fraction of the total, e.g., ~11% in Beijing-Tianjin-Hebei area (http://hbdczx.mep.gov.cn/pub/),

86   the emission factors of typical pollutants such as $PM_{2.5}$, organic carbon (OC) and polycyclic

87   aromatic hydrocarbons (PAHs) from farmers' coal stoves (about 1054-12910 mg/kg for $PM_{2.5}$, 470-

88   7820 mg/kg for OC and 58.5-229.1 mg/kg for PAHs) are usually about 1-3 orders of magnitude

89   greater than those from coal power plants or industries boilers (about 16-100 mg/kg for $PM_{2.5}$, 0.3-

90   17.1 mg/kg for OC and 0.8-12.8 μg/kg for PAHs) (Zhang et al., 2008; Xu et al., 2006; Geng et al.,

91   2014; Chen et al., 2005; Revuelta et al., 1999; Yang et al., 2016), and the coal consumption by

92   farmers mainly concentrates on the four months in winter.

93   In this study, to understand the possible influence of farmers' activities on the regional air quality in

94   the NCP, filter samples of $PM_{2.5}$ were collected daily in Beijing city as well as a rural area in Baoding,

95   Hebei Province for a whole year of 2014, and the seasonal variation characteristics of the water-

96   soluble ions (WSIs) in the $PM_{2.5}$ samples were comprehensively investigated in relation to the

97   farmers' activities. The scientific evidence found in this study will be helpful for future control

98   measures in reducing pollutant emissions from rural areas in the NCP.

99   **2. Materials and methods**

100   **2.1. Sampling sites**

101   The sampling site in Beijing city was on a rooftop (about 25 m above ground) in the Research Center

102   for Eco-Environmental Sciences (here referred to as RCEES, 40°00′29.85″N, 116°20′29.71″E),

103   which is located between the north fourth-ring road and the north fifth-ring road of Beijing and

104   surrounded by some institutes, campuses, and residential areas (Pang and Mu, 2006). Another

105   sampling site in a rural area was selected on the rooftop of a field station (about 5 m above ground)

106   which is located in the agricultural field of Dongbaituo village (here referred to as DBT,

107   38°39′37.36″N, 115°15′16.05″E), Baoding, Hebei Province. The rural sampling site is far away

108   from industries, traffic and commercial emissions. The distance between the two sampling sites is

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

110   **2.2. Sample collection**

111    $PM_{2.5}$ samples at the two sites were both collected on Millipore PTFE filters (90 mm) by a $PM_{2.5}$

112   sampler (LaoYing-2034) and the sampling flow rate was set to 100 L min^{-1}. The duration of each

113   sampling was 24 hours, started at 3:00 p.m. every day and ended at 3:00 p.m. on the next day. All

114   the samples were put in dedicated filter storage containers (90 mm, Millipore) after sampling and

115   preserved in a refrigerator till analysis. For the sampling site of RCEES, a total of 235 $PM_{2.5}$ samples

116   were collected from January to November of 2014, in winter (Jan 9- Mar 15), spring (Mar 16- May

117   31), summer (Jun 1- Jun 30, Aug 9- Aug 21) and autumn (Sep 19- Nov 14). To explore the possible

118   influence of farmers' activities, $PM_{2.5}$ samples at DBT were mainly collected during the periods of

119   periodic farmers' activities: heating season in winter (Jan 9- Feb 25), harvest seasons in summer

120   (Jun 9- Jun 22, Aug 9- Aug 17) and autumn (Sep 19- Oct 18, Oct 28- Nov 14).

121   **2.3. Sample analysis**

122   Each sample filter was extracted ultrasonically with 10 mL ultrapure water for half an hour. The

123   solutions were filtered through a micro-porous membrane (pore size, 0.45 μm; diameter, 13 mm)

124   before analysis and the WSIs in the treated filtrates were analyzed by Ion Chromatography (IC,

125   WAYEE IC6200). Five anions (F^-, $HCOO^-$, Cl^-, NO_3^- and SO_4^{2-}) were separated by using an anion

126   column (IC SI-52 4E, 4 mmID*250 mm) with the eluent (3.6 mmol L^{-1} Na_2CO_3) flow rate of 0.8

127 mL min^{-1} and column temperature of 45 ℃. Five cations (Na$^+$, NH$_4^+$, Mg^{2+}, Ca^{2+} and K$^+$) were

128 separated by using a cation column (TSKgelSuperIC-CR, 4.6 mmID*15 cm) with the eluent (2.2

129 mmol L^{-1} MSA and 1 mmol L^{-1} 18-crown-6) flow rate of 0.7 mL min^{-1} and column temperature of

130 40 ℃. The relative standard deviation (RSD) of each ion was less than 0.5% for the reproducibility

131 test. The detection limits (S/N=3) were less than 0.001 mg L^{-1} for the anions and cations. At least

132 three filter blanks were analyzed for 60 filter samples, and the average blank values were about 0.03

133 mg L^{-1} for Na$^+$, Ca^{2+}, F$^-$, NO$_3^-$ and SO$_4^{2-}$, 0.02 mg L^{-1} for NH$_4^+$ and Cl$^-$, 0.01 mg L^{-1} for Mg^{2+}, K$^+$

134 and HCOO$^-$. The concentrations of all the ions were corrected for blanks.

135 **2.4. Meteorology, trace gases and back trajectory**

136 The meteorological data, including temperature, wind speed, wind direction, relative humidity (RH),

137 visibility and Air Pollution Index of PM$_{2.5}$, SO$_2$, NO$_2$, O$_3$ at RCEES were from Beijing urban

138 ecosystem research station (http://www.bjurban.rcees.cas.cn/), which is about 20m away from our

139 sampling site of RCEES.

140 To identify the potential influence of air parcel transport, the air mass backward trajectories were

141 calculated for 72 h through the Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT

142 4) Model of the Air Resources Laboratory of NOAA with NCEP Final analyses data. The backward

143 trajectories arriving at 500 m above sampling position were computed at 0:00 h, 6:00 h, 12:00 h and

144 18:00 h (UTC) in each sampling day, respectively. A total of 940 backward trajectories with 72

145 hourly trajectory endpoints in four seasons were used as input for further analysis.

146 **3. Results and discussion**

147 The ratios of total cation concentration (defined as [Na$^+$] + [NH$_4^+$] + 2 ×[Mg^{2+}] +2 ×[Ca^{2+}] + [K$^+$])

148 to total anion concentration (defined as [F$^-$] + [HCOO$^-$] + [Cl$^-$] + [NO$_3^-$] + 2 ×[SO$_4^{2-}$]) in different

149   seasons are illustrated in Fig. 2a. The near unity of the ratios indicated excellent charge balance in

150     $PM_{2.5}$ and high quality of the data. The mass concentrations of WSIs and $PM_{2.5}$ at the sampling site

151   of RCEES during the period of Jan 1- Jan 24, 2015 were also simultaneously measured by the filter

152   sampling method and the TEOM 1405 Monitor, respectively. As shown in Fig. 2b, the variation

153   trends of the WSIs and $PM_{2.5}$ were almost the same with a correlation coefficient (R^2) of 0.91,

154   implying that the concentration of WSIs measured could be used as an indicator of the pollution

155   level. The average mass concentration of WSIs contributed about 80% to the mass of $PM_{2.5}$

156   measured by the TEOM 1405 Monitor, which was much greater than the values of 50-60% reported

157   by previous studies in the NCP (Shen et al., 2009;Li et al., 2013). It was possible that the mass

158   concentration of $PM_{2.5}$ measured by the TEOM 1405 Monitor was underestimated because the

159   volatile even semi-volatile component in $PM_{2.5}$ can be easily lost at 50 ℃ which is designed in the

160   TEOM 1405 Monitor for avoiding water condensation on the filter (Charron et al., 2004; Grover et

161   al., 2005;Liu et al., 2014). It is well documented that temperature is a key factor affecting the

162   distribution of NH_4NO_3 on particle phase due to its thermal decomposition, e.g., at temperature

163   greater than 35 ℃, little NH_4NO_3 is expected under typical ambient conditions (Finlayson-Pitts et

164   al., 1986). The total mass proportions of NO_3^- and NH_4^+ in WSIs usually account for about 50% in

165   Beijing city (Yang et al., 2015a), whereas they were found to only account for about 20% in the

166   filters of the TEOM 1405 Monitor in this study, confirming the serious loss of NH_4NO_3 under the

167   high temperature adopted by the TEOM 1405 Monitor.

168   **3.1. Daily variations of WSIs in Beijing city**

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

170   concentrations of the WSIs at RCEES are summarized in Table 1. It is evident that the concentration

171 of the WSIs varied greatly on timescale of days, indicating meteorological conditions played a

172 pivotal role in accumulation and dissipation of atmospheric pollutants. For example, the highest

173 frequency pollution levels of the WSIs in winter were mainly ascribed to the relatively stable

174 meteorological conditions with the low height of boundary layer which favored pollutants'

175 accumulation (Wang et al., 2013;Quan et al., 2014;Tian et al., 2014;Wang et al., 2014;Zhang et al.,

176 2015a). Besides meteorological conditions, the extremely high levels of the WSIs during the

177 pollution episodes revealed strong sources of the pollutants around Beijing.

178 The mean concentrations ($\mu g\ m^{-3}$) of WSIs at RCEES in spring, summer, autumn and winter were

179 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

180 found to be the principal ions, accounted for about 80% to the total WSIs in each season, which

181 were in line with previous studies (Hu et al., 2014;Yang et al., 2015a;Huang et al., 2016;Yang et al.,

182 2015b). The three principal ions were mainly ascribed to secondary formation as discussed in the

183 following section. Although the most intensive photochemical reactivity in summer favors sulfate

184 and nitrate formation, the relatively low SO_2 concentration, the reduced gas-to-particle partitioning

185 of ammonium nitrate and the frequent scavenging by rain events must greatly counteract the

186 contribution of the secondary formation, resulting in the lowest pollution levels of the WSIs in

187 summer. In comparison with other seasons, the large elevation of atmospheric SO_2 and NO_x (see

188 section 3.2.3) in winter would result in large sulfate and nitrate formation rates despite the lower

189 concentrations of oxidizing species and cause the highest mean concentration of WSIs. Although

190 the atmospheric concentrations of SO_2 and NO_x in autumn were much smaller than in winter and in

191 spring (see section 3.2.3), the mean concentration of WSIs in autumn was almost the same as that

192 in winter and nearly twice as those in spring and summer, indicating that special mechanisms

193   dominated the secondary formation of the atmospheric principal ions (see section 3.2.3).

194   **3.2. The possible sources for the WSIs**

195   To explore the possible contribution of the periodic emissions from farmers' activities to the WSIs

196   in Beijing, the concentrations of typical WSIs at the urban and rural sites are compared in Fig. 4. It

197   is evident that the seasonal variation of the typical WSIs at the two sites exhibited the similar trend,

198   indicating the similar regional meteorological conditions. The concentrations of the typical WSIs at

199   DBT were generally higher than those at RCEES during the periods of farmers' activities (heating

200   in winter, fertilization in summer and maize harvest in autumn). To reveal the air mass transport

201   influence on the WSIs in Beijing, three-day backward trajectories for clusters and the corresponding

202   mass concentrations of WSIs during the four seasons in Beijing were analyzed, and the results are

203   illustrated in Fig. 5. It could be seen that the highest concentrations of the typical WSIs were usually

204   observed in the air parcels from southwest/south regions with high density of population.

205   Considering the large fraction (~30%) of air parcels from the southwest/south regions in each season,

206   the human activities in the southwest/south regions contributed to the atmospheric WSIs in Beijing.

207   Besides the industries, the emissions from the high density of farmers in the southwest/south regions

208   of Beijing was also suspected to affect to the atmospheric WSIs in Beijing.

209   3.2.1. The sources of K^+ and Cl^-

210   With the exception of the extremely high concentrations of K^+ on 1 February and 16 February (Fig.

211   4) due to firework for celebrating Spring Festival and Lantern Festival (Jiang et al., 2015;Kong et

212   al., 2015), the concentrations of Cl^- and K^+ were much higher in winter and autumn than in spring

213   and summer at the two sites (Fig. 4). The molar ratio of Cl^- to Na^+ at the two sites measured by this

214   study (Fig. 6) in each season was above 1.30 which was greater than the value of 1.18 in fresh sea-

215   salt particles (Brewer, 1975), indicating sources other than sea-salt dominated atmospheric Cl^-. The

216   pronounced correlation coefficients ($r > 0.6$, $p < 0.01$) between K^+ (the indicator for biomass burning,

217   Gao et al., 2011) and Cl^- in winter and autumn indicated that crop straw burning was a common

218   source for K^+ and Cl^- (Li et al., 2014). However, only crop straw burning couldn't explain the

219   relatively high concentrations of Cl^- in winter (Fig. 4), because the average molar Cl^-/K^+ ratio of 7.8

220   (except for firework event during the Spring Festival) in winter was about a factor of 2 greater than

221   the value of 4.2 in autumn when straw burning was prevailing in the region. Besides straw burning

222   and sea-salt, coal combustion (Yu et al., 2013;Wu et al., 2014) and biofuel burning (Christian et al.,

223   2010) have been also recognized as the sources for atmospheric Cl^-. Coal have almost been replaced

224   with natural gas and electricity for heating during the winter before 2013 in Beijing city (Ma et al.,

225   2015). Considering the relatively stable Cl^- emissions from coal combustion of industries and power

226   plants as well as biofuel burning during the whole year, the obviously higher Cl^- concentrations

227   measured in winter than in other seasons (Fig. 4) should be ascribed to the additional coal

228   combustion by farmers because of the large amount of residential coal consumption (about 42

229   Tg/year) in Beijing-Tianjin-Hebei region and extremely high emission factors of Cl^- (80-300 mg/kg

230   coal) from the coal combustion (Huang et al., 2014b). The obviously higher Cl^- proportion in winter

231   than in early spring (Fig. 7) provided further evidence for the above conclusion, because the

232   proportion largely counteracted the influence of meteorological factors.

233   It is interesting to note that the remarkably higher Cl^-/Na^+ ratio was observed in summer than in

234   other seasons at RCEES (Fig. 6), which couldn't be explained by the Cl^- sources mentioned above.

235   Fertilization events in the vast agricultural fields of the NCP were suspected to contribute to

236   atmospheric Cl^- in Beijing because volatile NH_4Cl fertilizer are prevailingly used as the basal

237 fertilization for maize in summer. Based on yearbook of China fertilizer industry (2012), national

238 production of NH_4Cl fertilizers was about 1.174 Tg in 2011, which was mainly used as the basal

239 fertilization for maize in summer. The obviously high concentrations of Cl^- at DBT (Fig. 4) were

240 indeed observed during the basal fertilization period for maize in June. Compared with the periods

241 before and after maize fertilization, the proportion of Cl^- during maize fertilization in summer

242 increased about 3%-4% (Fig. 7), confirming the influence of maize fertilization on atmospheric Cl^-

243 in Beijing. The extremely high concentration (about 2 ppbv) of Nitryl chloride ($ClNO_2$) observed

244 by Tham et al. (2016) at the same rural site in June indirectly indicated the high concentrations of

245 Cl^- during the period of basal fertilization for maize. Because fertilization is an important source for

246 atmospheric NH_3, the elevation of Cl^- (as a tracer for fertilization) revealed that fertilization in the

247 rural areas around Beijing could also make obvious contribution to atmospheric NH_4^+ in Beijing.

248 3.2.2. The sources of Ca^{2+}

249 The remarkably high concentrations of Ca^{2+} occurred in both spring and autumn at RCEES (Fig. 3

250 and Fig. 4), which were in good agreement with previous studies (Fig. 8). The evident elevation of

251 Ca^{2+} concentrations in spring has been usually ascribed to the frequent dust storms (Zhao et al.,

252 2013b), but there was still no explanation about the extremely high Ca^{2+} concentrations in autumn

253 (Zhao et al., 2013b;Zhang et al., 2013). The intensive maize harvest and soil ploughing in autumn

254 in the vast agricultural fields of the NCP were suspected to contribute to atmospheric Ca^{2+} in Beijing.

255 Because abundant atmospheric mineral particles were absorbed by crop leaves (Bealey et al., 2007;

256 Ji et al., 2013) during crop growing season, especially in the North China where atmospheric mineral

257 dust is always at high level (Zhang et al., 2013;Zhao et al., 2013b), a large fraction of the mineral

258 dust absorbed on the leaves of crop could be released into the atmosphere during harvest with crop

259   straw being crushed into pieces for returning to fields which is a prevailing method under the

260   advocacy of governments for reducing the influence of crop straw burning on the air quality.

261   Additionally, the soil ploughing can also cause the suspension of particles (Fang et al., 2006; Chen

262   et al., 2015). The remarkably high concentrations of Ca^{2+} during the autumn at DBT (Fig. 4) should

263   be ascribed to the above agricultural activities because there are few construction activities in the

264   rural area. Compared with the periods before and after maize harvest and soil ploughing, the

265   proportion of Ca^{2+} during maize harvest and soil ploughing in autumn increased about 5%-7% (Fig.

266   7), confirming the influence of maize harvest and soil ploughing on atmospheric Ca^{2+} in Beijing.

267   The back trajectory cluster analysis also supported the above conclusion: (1) the extremely high

268   concentrations of Ca^{2+} in Beijing occurred during the period of 6-25 October (Fig. 3 and Fig. 4)

269   when the air parcels were mainly from the southwest/south regions (Fig. 5) where the vast areas of

270   agricultural field were being under intensive maize harvest and soil ploughing. (2) Although the

271   concentrations of Ca^{2+} in the rural area remained at high levels during the period of 2-14 November

272   (Fig.3 and Fig. 4), the relatively low concentrations of Ca^{2+} in Beijing were observed during the

273   period when the air parcels were mainly from the northwest region (Fig. 5) where agricultural

274   activities are relatively sparse.

275   3.2.3. The sources of NH_4^+, SO_4^{2-} and NO_3^-

276   The remarkably high concentrations of NH_4^+, SO_4^{2-} and NO_3^- also appeared in both winter and

277   autumn at the two sites (Fig. 4). NH_4^+ was mainly from the reactions of NH_3 with acid gases (such

278   as HNO_3) and acid particles, and hence its variation trend was the same as those of SO_4^{2-} and NO_3^-.

279   Although atmospheric NH_3 has long been considered to be mainly from agricultural activities, their

280   emissions mainly concentrate on warmer seasons (Krupa, 2003), which cannot explain the frequent

281 high concentrations of NH_4^+ observed in winter. Besides the increased gas-to-particle partitioning

282 of ammonium nitrate at lower temperatures, strong NH_3 emission sources other than agricultural

283 activities were suspected to be responsible for the frequent high concentrations of NH_4^+ in the cold

284 winter. Besides NH_3 emission from vehicles (Liu et al., 2014), strong emission of NH_3 from farmers'

285 coal stoves (the NH_3 emission factor was 0.62-1.10 g/kg coal) was indeed found by our preliminary

286 measurements, which was in line with the latest study (Li et al., 2016). During the serious pollution

287 episodes, the concentrations of SO_2 at RCEES in autumn were almost the same as those in summer

288 and about one order of magnitude lower than in winter (Fig. 9), but the peak concentrations of SO_4^{2-}

289 in autumn were about a factor of 2 greater than those in summer and at almost the same level as

290 those in winter. The gaseous phase reaction with OH (Zhao et al., 2013c;Quan et al., 2014), the

291 heterogeneous reaction on mineral dust (He et al., 2014;Nie et al., 2014), and multiphase reactions

292 in the aerosol water (Zheng et al., 2015a) of SO_2 have been recognized to be responsible for

293 atmospheric SO_4^{2-} formation. The significant elevation of both Ca^{2+} and SO_4^{2-} in autumn implied

294 that the heterogeneous reaction of SO_2 on the mineral dust might greatly accelerate the conversion

295 of SO_2 to SO_4^{2-}. Although evidently high concentrations of Ca^{2+} occurred (Fig. 3 and Fig. 4) in

296 spring and SO_2 concentrations were much greater in spring than in autumn (Fig. 9), the SO_4^{2-}

297 concentrations were about a factor of 2 less in spring than in autumn. Atmospheric humidity was

298 suspected to play an important role in the heterogeneous reaction, e.g., the relative humidity was

299 much higher in autumn than in spring during the serious pollution events (Fig. 9). Similar to SO_4^{2-},

300 the relatively high concentrations of NO_3^- during the serious pollution events in autumn were also

301 ascribed to the heterogeneous reaction of NO_2 on the mineral dust. Therefore, the emission of

302 mineral dust from maize harvest and soil ploughing in autumn also played important roles in

303   secondary formation of nitrate and sulfate in Beijing.

304   The nitrogen oxidation ratio NOR = nNO_3^- / (nNO_3^- + nNO_x) (n refers to molar concentration) and

305   the sulfur oxidation ratio SOR = nSO_4^{2-} / (nSO_4^{2-} + nSO_2) have been used to estimate the degree of

306   secondary formation of NO_3^- and SO_4^{2-}, which can counteract the interference of meteorological

307   factors (Chan and Yao, 2008;Yu et al., 2013;Guo et al., 2014;Huang et al., 2014a;Yang et al.,

308   2015b;Zheng et al., 2015b). The values of NOR and SOR during haze days and non-haze days in

309   four seasons are listed in Table 2. Both the values of NOR and SOR on non-haze days were found

310   to be the highest in summer and the lowest in winter, reflecting the seasonal variation of

311   photochemical intensity. Although sunlight intensity greatly reduced at ground level during haze

312   days, the values of NOR and SOR were about a factor of 2 greater during haze days than during

313   non-haze days in the four seasons, implying again that the heterogeneous or multiphase reactions of

314   SO_2 and NO_2 on atmospheric particles made significant contribution to atmospheric sulfate and

315   nitrate.

316   3.2.4. The variation characteristics of NO_3^- and SO_4^{2-} during serious pollution episodes

317   As shown in Fig. 9, the serious pollution episodes with noticeable elevation of various pollutants

318   usually occurred under slow wind speed (less than 2 m s^{-1}) and high relative humidity. In comparison

319   with their precursors of SO_2 and NO_x, the detailed variation trends of SO_4^{2-} and NO_3^- were different,

320   indicating that the elevation of SO_4^{2-} and NO_3^- was not simply ascribed to the physical process of

321   accumulation. It is interesting to note that the increasing rates of SO_4^{2-} during some serious pollution

322   events especially with elevation of Ca^{2+} (such as in spring and autumn) were much slower than those

323   of NO_3^- (Fig. 10), implying that the atmospheric heterogeneous reaction of NO_2 on the mineral dust

324   was faster than that of SO_2. Compared with summer and winter, the relatively high ratios of NO_3^-

325   /SO$_4^{2-}$ in spring and autumn (Fig. 6) also supported the above conclusion.

326   **3.3. Comparison with previous studies**

327   The mean concentrations of the three principal ions and some related indicators in Beijing over the

328   past decade are summarized in Table 3. The seasonal variations of the three principal ions reported

329   were quite different, e.g., Huang et al. (2016) found the maximal mean concentrations of SO$_4^{2-}$ and

330   NH$_4^+$ in the summer and of NO$_3^-$ in the autumn of 2014, whereas in this study all the maximal mean

331   concentrations of the three principal ions appeared in autumn. The mean concentrations of the three

332   ions in autumn in this study were in good agreement with the values reported by Yang et al. (2015).

333   For the molar concentration ratios of NO$_3^-$/SO$_4^{2-}$ (denoted as N/S), all the investigations exhibited

334   relatively high values in autumn and spring, further confirming that the heterogeneous reaction of

335   NO$_2$ on mineral dust favored nitrate formation (as discussed above). For NOR and SOR, all

336   investigations were in good agreement, with the highest values in summer, the lowest in winter and

337   higher values during haze days than during clean days. Compared with the investigations of 2003,

338   the evident increase of both the concentration of NO$_3^-$ and the ratio of N/S in recent years revealed

339   the fast increase of vehicle numbers in the decade made significant contribution to atmospheric

340   nitrate.

341   **4. Conclusions**

342   The large daily fluctuation of the WSIs in each season confirmed that meteorological factors played

343   an important role in governing the accumulation and dispersion of the pollutants. The extremely

344   high concentrations of the WSIs during the serious pollution episodes indicated there were strong

345   sources of the pollutants in Beijing. Based on the comprehensive analysis of the data of the WSIs,

346   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, the strong emissions of pollutants from the periodic

activities of farmers should be paid greater attention.

Author contribution

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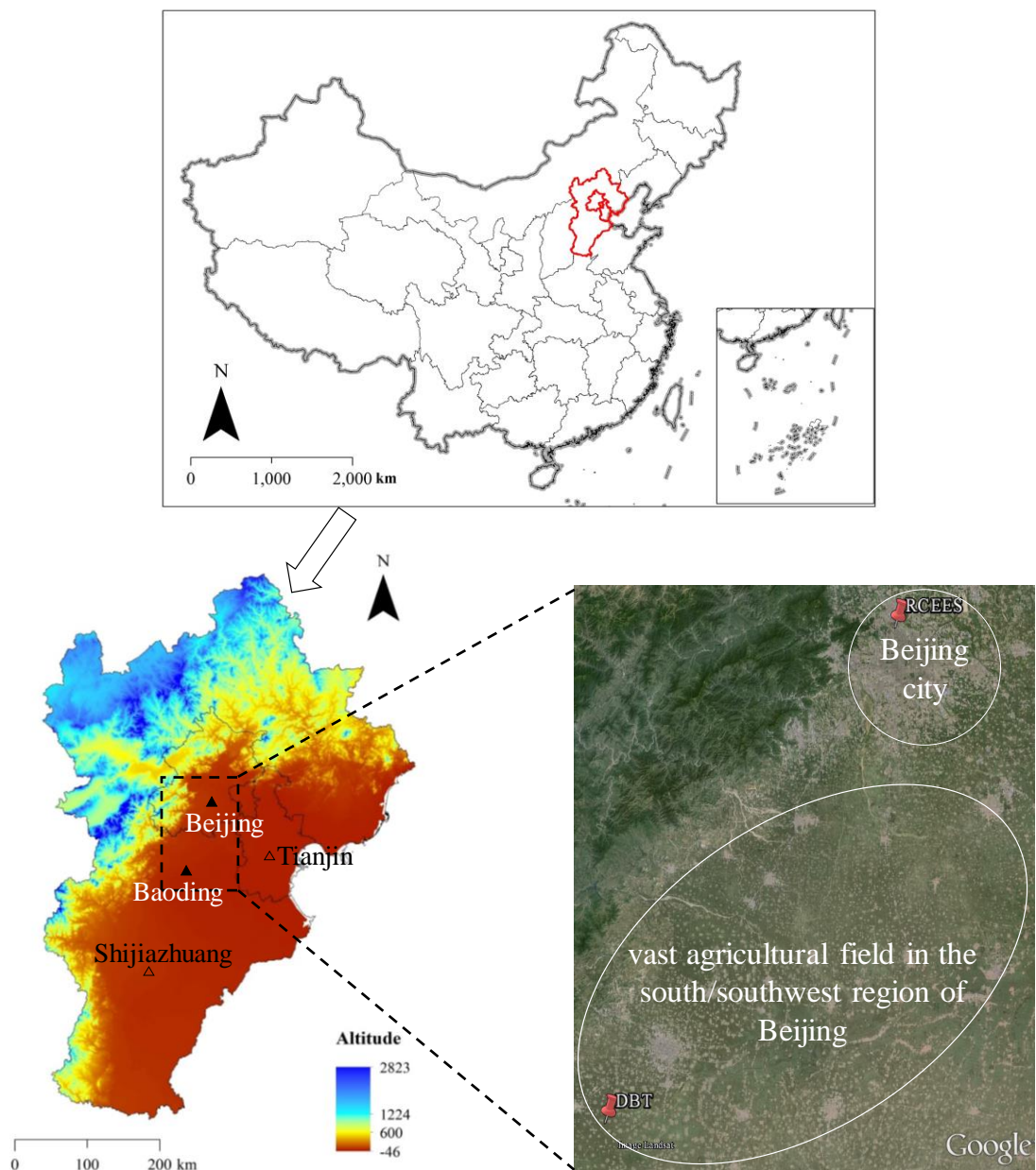
587   **Fig. 1** Sampling sites (the urban site in Beijing city and the rural site in Baoding, Hebei Province) in the NCP.

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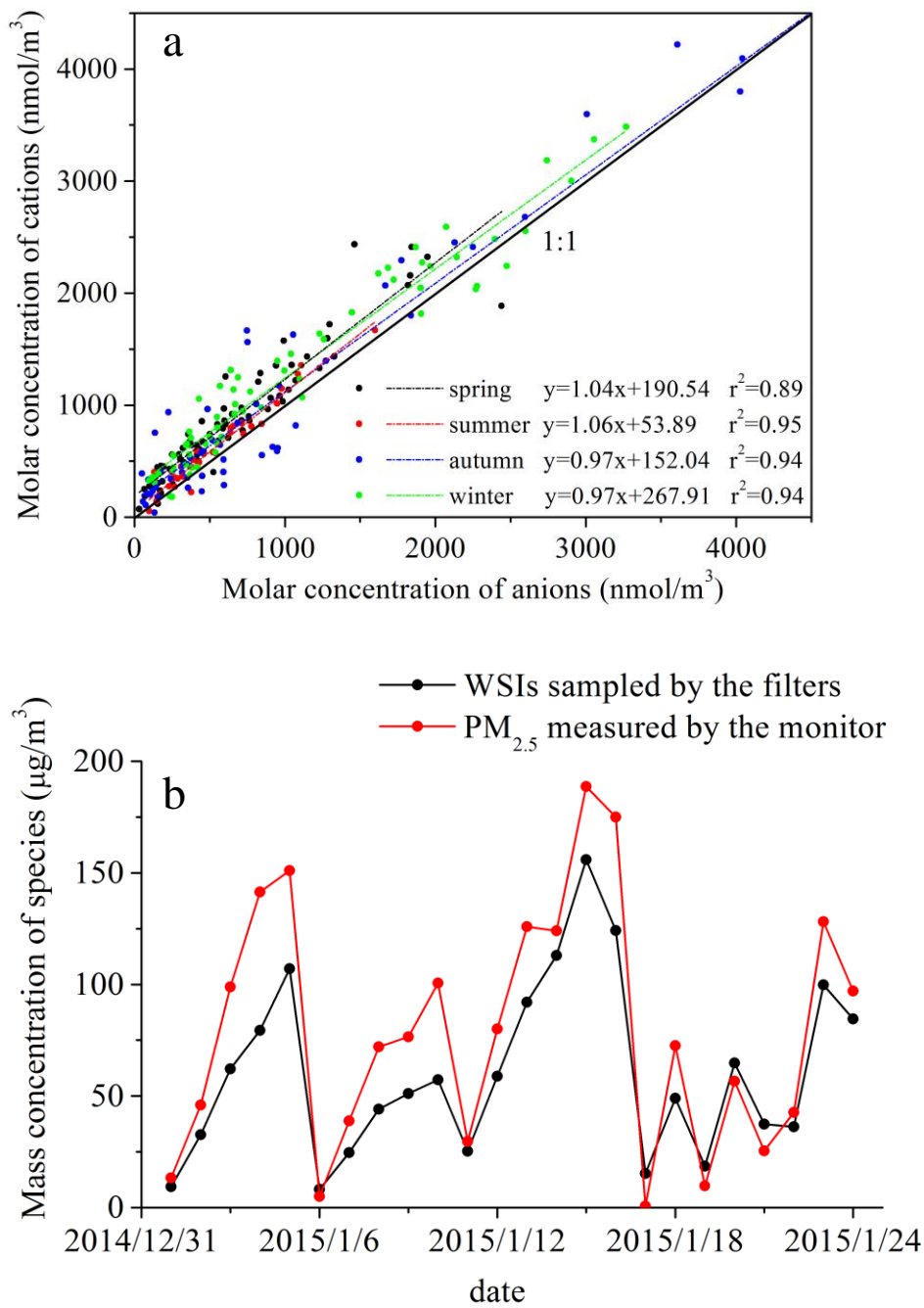
591 **Fig. 2** The ratios of cations to anions in the four seasons of 2014 in Beijing (Fig. 2a), and the comparison between

592 WSIs sampled by the filters and PM$_{2.5}$ measured by the TEOM monitor (Fig. 2b, 1-24 January, 2015).

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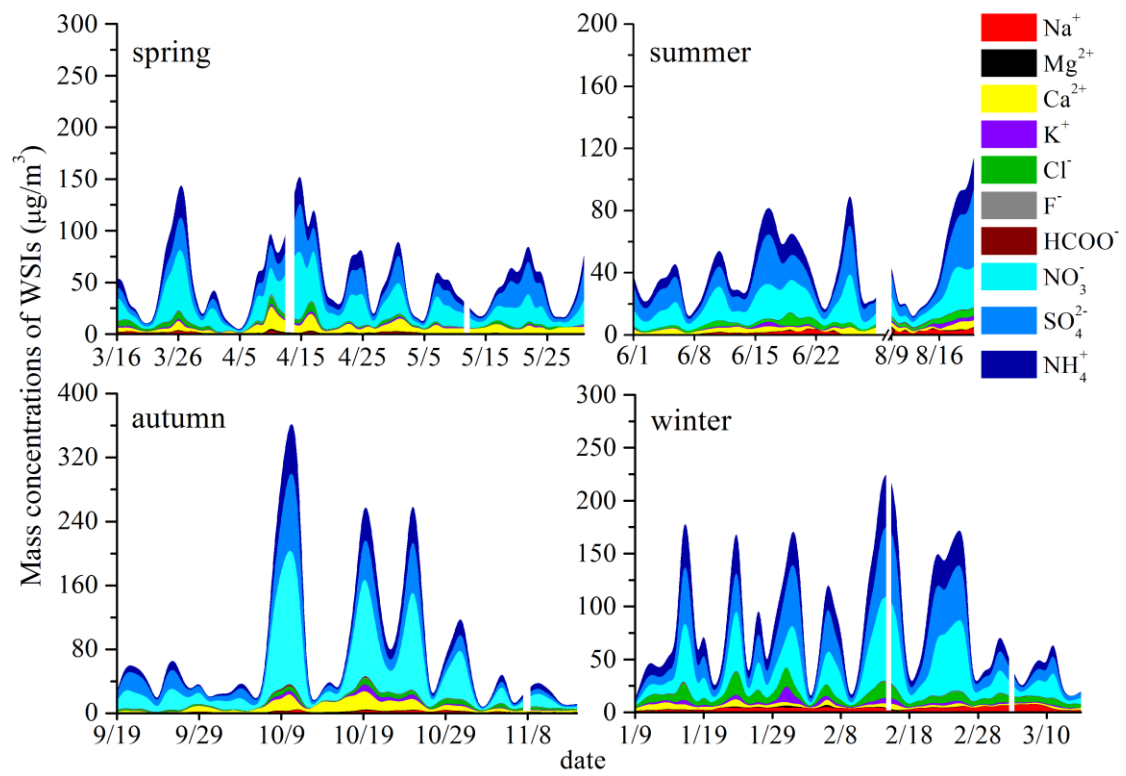
Fig. 3 Variation of WSIs in each season at RCEES (the smooth lines for the WSIs were drawn between the points
of the daily data.).

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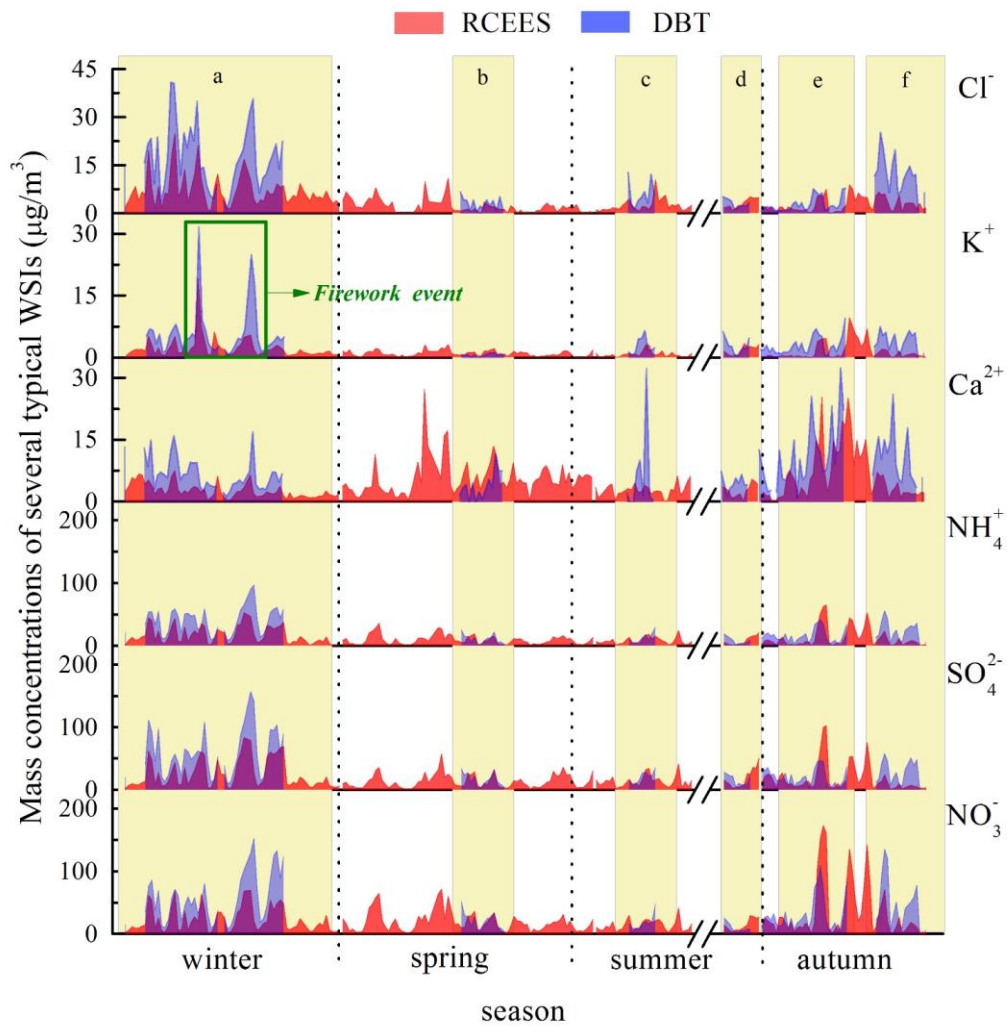
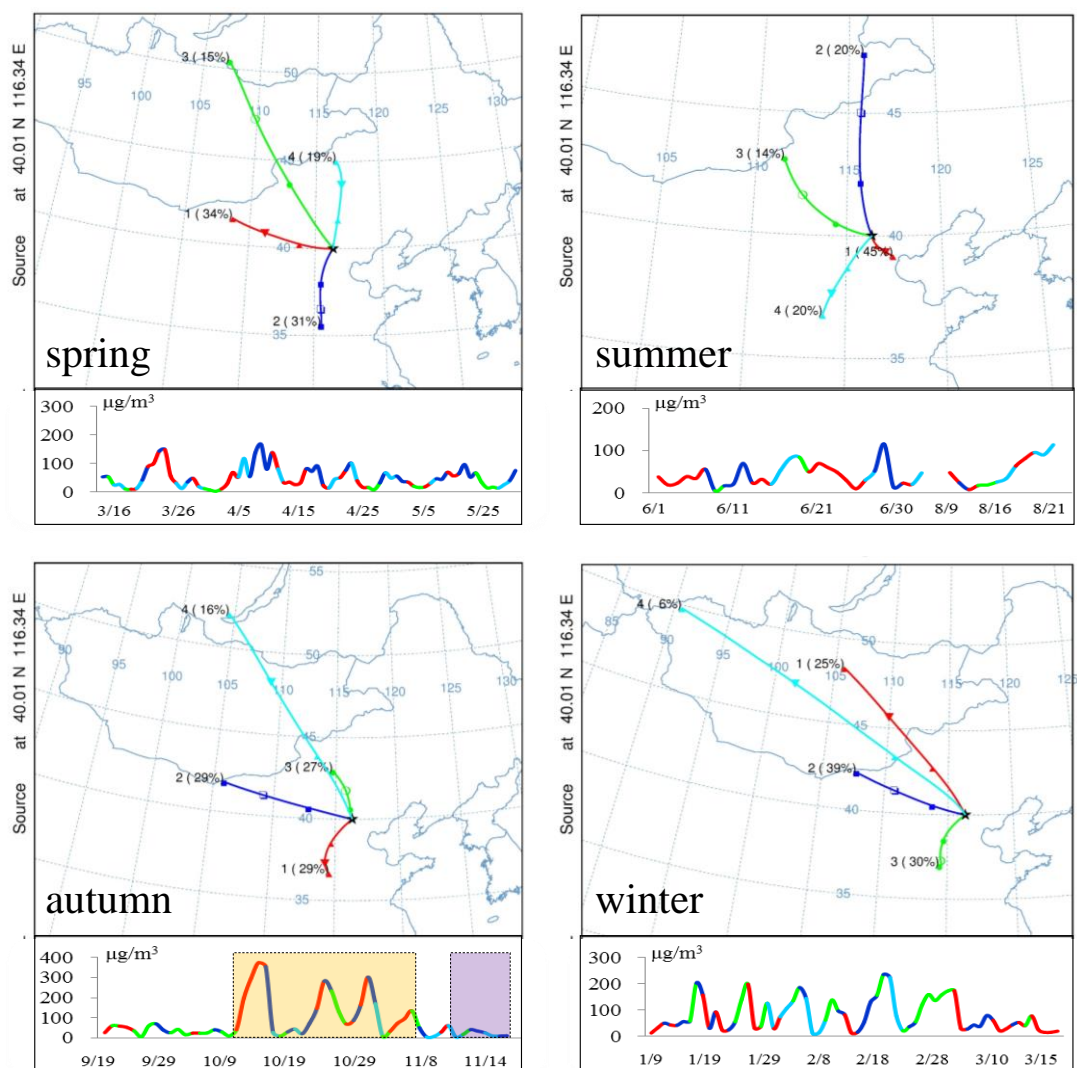


Fig. 4 Concentrations of selected WSIs in the year of 2014. (The mass concentrations of Cl⁻, K⁺, Ca²⁺, NH₄⁺, SO₄²⁻ and NO₃⁻ were presented at RCEES and DBT. The green square shows the firework event during the period of the Spring Festival. The areas shaded in yellow represent farmers' activities, including 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).)

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

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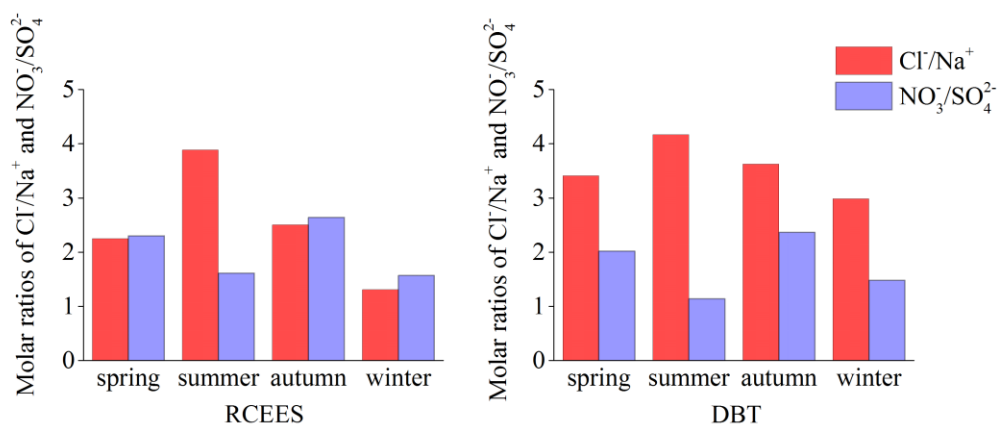
        Fig. 6 The average molar ratios of Cl⁻/Na⁺ and NO₃⁻/SO₄²⁻ in each season at the two sites.

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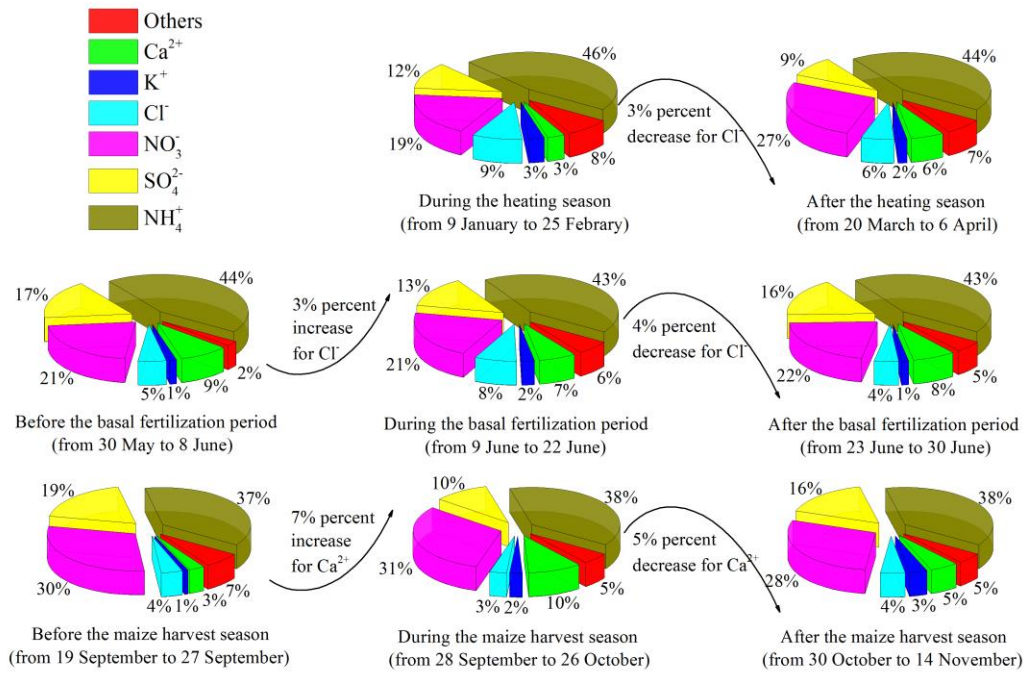
620   **Fig. 7** Molar fractions of atmospheric WSIs at RCEES before, during and after the periods of heating in winter,

621   maize fertilization in summer, and maize harvest and soil ploughing in autumn.

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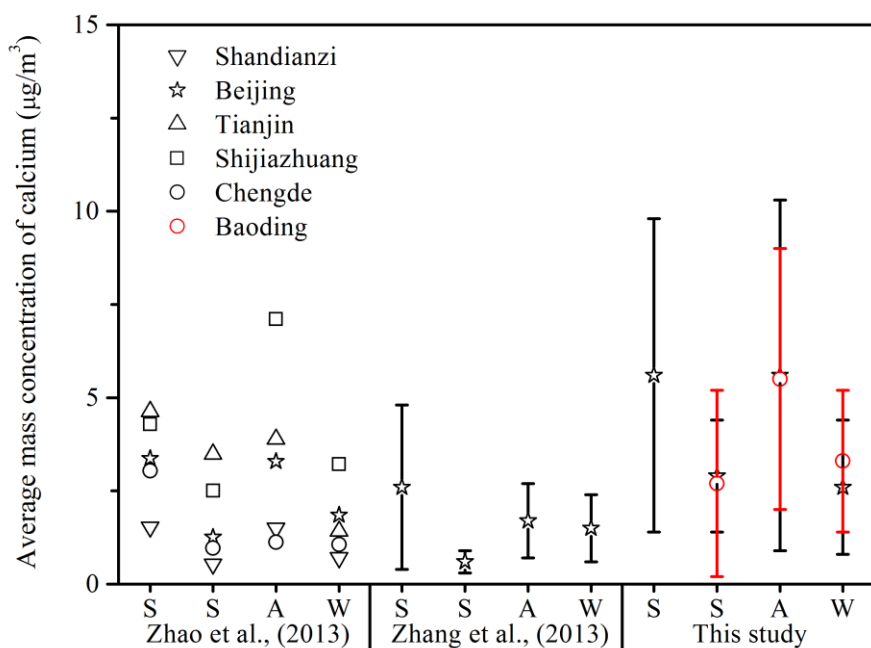
625 **Fig. 8** Comparison of average mass concentrations of calcium in four seasons between previous studies and this

626 study for several cities in the NCP (S, S, A and W represent spring, summer, autumn and winter, respectively. The

627 black symbols represent the urban sites and the red symbol represents the rural site (DBT).).

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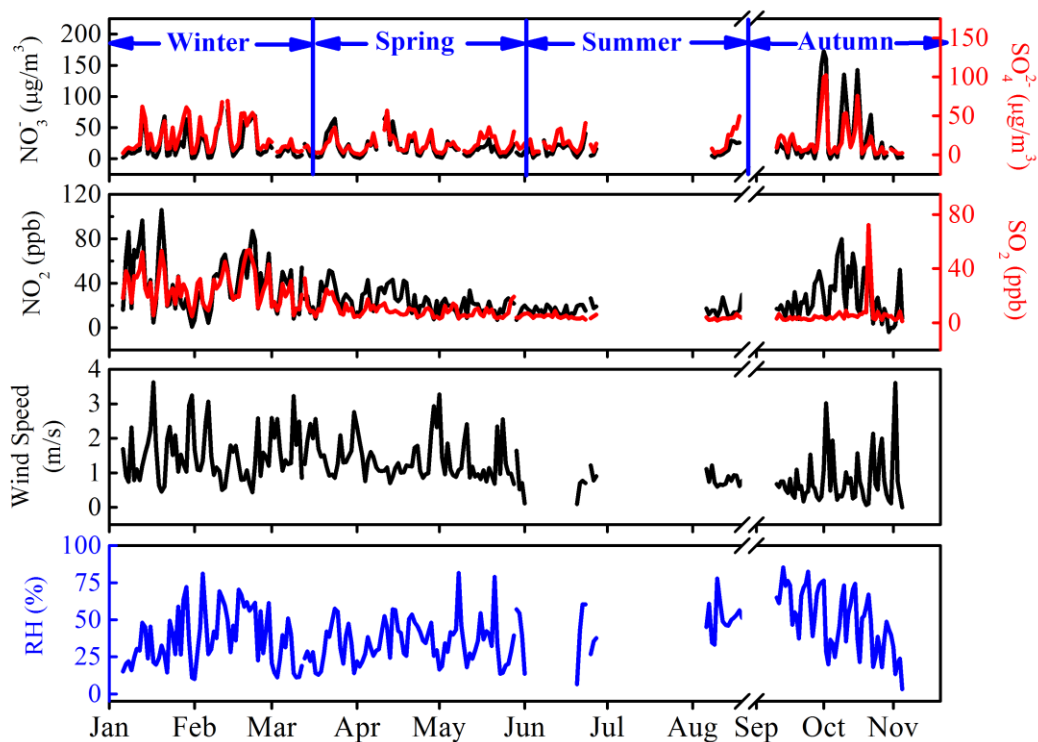
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631 **Fig. 9** Time series of NO_3^-, SO_4^{2-}, NO_2 and SO_2 and meteorological data (wind speed and relative humidity) during

                          the four seasons in Beijing for 2014

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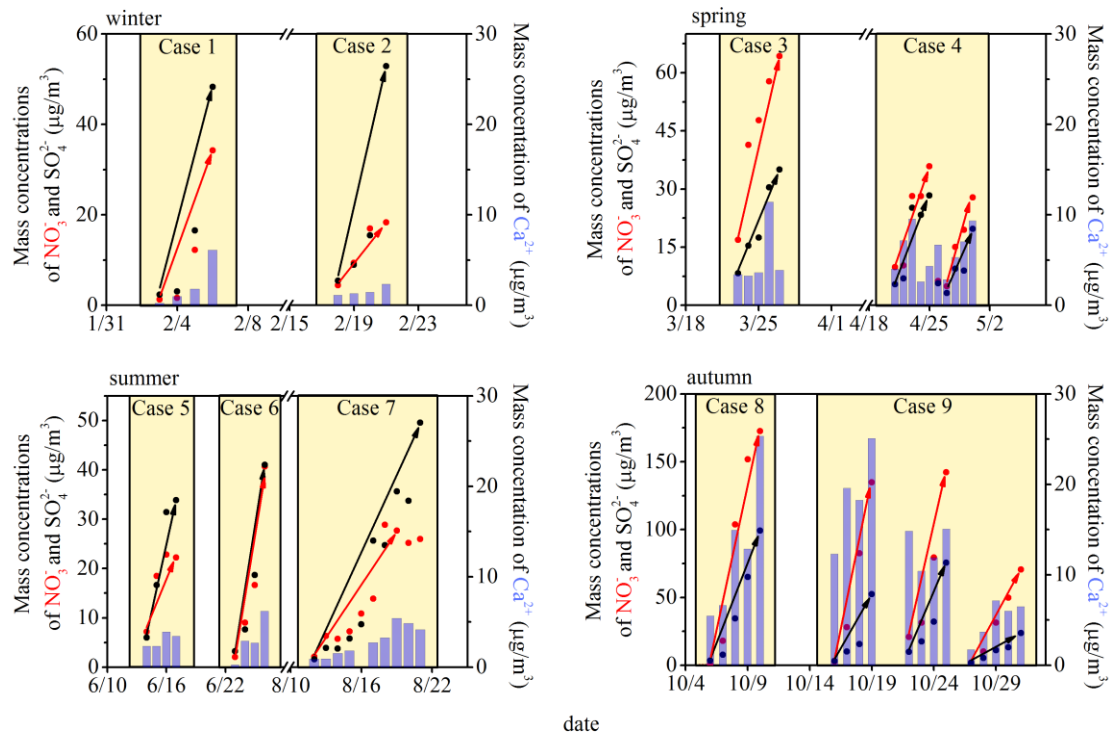
636   **Fig. 10** Case studies about the increasing rates of NO_3^- and SO_4^{2-} with the elevation of Ca^{2+} during serious

637   pollution events in the four seasons.

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

641   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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644   **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

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

Table 3 Summary of three principal ions (μg m^{-3}), the molar 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	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													35.5	20.0	16.7	2.8	0.2	0.4							Yang et al., 2015b
2013-2014(haze)	14.7	9.0	10.3	2.5	0.2	0.4	33.9	32.7	24.0	1.5	0.3	0.7	40.0	17.4	22.2	3.6	0.2	0.6	22.0	20.4	18.8	1.7	0.2	0.2	Huang et al., 2016
2013-2014(clean)	3.6	2.4	4.4	2.3	0.1	0.2	8.8	8.1	11.7	1.7	0.1	0.4	5.5	4.5	5.6	1.9	0.1	0.4	6.6	5.2	6.0	2.0	0.1	0.1	Huang et al., 2016
2013(haze)	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	26.1	33.3	24.1	1.2	-	-	Tian et al., 2014
2013(clean)	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	4.9	5.0	4.9	1.5	-	-	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	1.7	-	-	11.8	23.5	11.0	0.8	-	-	10.7	7.9	4.7	2.2	-	-	7.3	8.5	4.5	1.4	-	-	Zhang et al., 2013
2009	-	-	-	-	-	-	12.7	26.1	9.1	0.8	0.2	0.7	6.1	20.1	4.3	0.5	0.1	0.6	-	-	-	-	-	-	Hu et al., 2014
2005	-	-	-	-	-	-	9.9	22.6	4.7	0.6	-	-	-	-	-	-	-	-	-	-	-	-	-	-	Pathak et al., 2009
2001-2003	11.9	13.5	6.5	1.4	0.1	0.1	11.2	18.4	10.1	0.9	0.1	0.4	9.1	12.7	6.3	1.1	0.1	0.2	12.3	21.0	10.6	0.9	0.1	0.1	Wang et al., 2005
2002-2003	-	-	-	-	-	-	12.2	16.0	10.4	1.2	-	-	-	-	-	-	-	-	17.0	30.4	12.9	0.9	-	-	Sun et al., 2004