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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 atmospheric fine particles called $PM_{2.5}$. To mitigate the serious pollution status, identification of the sources of $PM_{2.5}$ is urgently needed for the effective control measures. A total of 235 daily samples of $PM_{2.5}$ were collected in Beijing through the year of 2014, and the 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 unusually high ratio of Cl^- to Na^+ in summer could be rationally explained by the prevailing fertilization of NH_4Cl for planting summer maize in the vast area of NCP. The remarkable elevation of Cl^- in winter was ascribed to coal combustion for heating by farmers. The most serious pollution episodes in autumn were coincident with significant elevation of Ca^{2+} which was ascribed to be from harvest of the summer maize and tillage for planting the winter wheat. The mineral dust emission from the harvest and tillage 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 relatively high concentration of K^+ in winter and autumn further confirmed that crop straw burning made evident contribution to atmospheric $PM_{2.5}$ in Beijing. 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., 2014;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

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particulate matter, usually called $PM_{2.5}$ (Huang et al., 2014). $PM_{2.5}$ 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., 2014), principal component analysis (PCA) (Wang et al., 2015) and chemical mass balance (CMB) (Huang et al., 2014;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 (Huang et al., 2014). 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 domestic coal stoves on both the emission strengths 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

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mainly focus on June-July and October-November and domestic 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 totally 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, 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 domestic 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 strengths of pollutants from farmers' coal stove is usually about 1-2 magnitude greater than those from power plants (Xu et al., 2006), and the farmers coal consumption mainly concentrates on the four months in winter.

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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 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

The sampling site was chosen on a rooftop (about 25m above ground) in the Research Center for Eco-Environmental Sciences (RCEES), 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). $PM_{2.5}$ samples were collected on Millipore PTFE filters (90mm) by an artificial intelligence's $PM_{2.5}$ sampler (LaoYing-2034) and the sampling flow rate was set to 100L min^{-1}. The duration of each sampling was 24 hours, started at 3:00 p.m. every day and ended at 3:00 p.m. on the next day. All the samples were put in dedicated filter storage containers (90mm, Millipore) after sampling and preserved in a refrigerator till analysis. A total of 235 $PM_{2.5}$ samples were collected from January to November of 2014, in winter (Jan 9- Mar 15 2014), spring (Mar 16- May 31 2014), summer (Jun 1- Jun 30, Aug 9- Aug 21 2014) and autumn (Sep 19- Nov 14 2014).

2.2. Ion analysis

Sample and blank filters were extracted ultrasonically with 10mL ultrapure water for half an hour. The solutions were filtered through water micro-porous membrane (pore size, 0.45μm; diameter, 13mm) before analysis and the water-soluble ions (WSIs) in the treated filtrates were analyzed by

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Ion Chromatography (IC, WAYEE IC6200). Five anions (F^-, $HCOO^-$, Cl^-, NO_3^- and SO_4^{2-}) were separated by using an anion column (IC SI-52 4E, 4mmID*250mm) with the eluent (3.6mmol L^{-1} Na_2CO_3) flow rate of 0.8mL min^{-1} and column temperature of 45 ℃. Five cations (Na^+, NH_4^+, Mg^{2+}, Ca^{2+} and K^+) were separated by using a cation column (TSKgelSuperIC-CR, 4.6mmID*15cm) with the eluent (2.2mmol L^{-1} MSA and 1mmol L^{-1} 18-crown-6) flow rate of 0.7mL min^{-1} and column temperature of 40 ℃. 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. The concentrations of all the ions (less than 0.03 mg L^{-1} for each ion) in daily field blank filter were subtracted from sample determination.

2.3. 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 in RCEES were both collected from Beijing urban ecosystem research station (http://www.bjurban.rcees.cas.cn/).

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) 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.

2.4 The TEOM 1405 Monitor

The mass concentration of $PM_{2.5}$ was monitored by a tapered element oscillating microbalance with the filter dynamic measurement system (TEOM-FDMS, Thermo; Model 1405). A filter in the

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TEOM 1405 Monitor is used for collecting and measuring $PM_{2.5}$ through variation of the oscillation frequency. To avoid water condensation on the TEOM filter, the temperature of the TEOM filter as well as the inlet is kept at 50 ℃ during sampling. In this study, we replaced the TEOM filters every 12 days, and the concentrations of the WSIs on the TEOM filters were analyzed for comparing with those on the filter collected by the filter sampling method.

3. Results and discussion

3.1. Comparison between WSIs and $PM_{2.5}$

The mass concentrations of WSIs and $PM_{2.5}$ at the sampling site were simultaneously measured by the filter sampling method and the TEOM 1405 Monitor for 24 days (Jan 1- Jan 24, 2015). As shown in Fig. 1a and Fig. 1b, the variation trends of the WSIs and $PM_{2.5}$ were almost the same with a correlation coefficient (R^2) of 0.908, implying that the concentration of WSIs measured could well reveal the pollution status of $PM_{2.5}$ in Beijing. The average mass concentration of WSIs contributed about 80% to the mass of $PM_{2.5}$ measured by the TEOM 1405 Monitor, whereas the WSIs accounted for about 50-60% of the total mass concentration measured by the filter sampling method in the NCP (Shen et al., 2009;Li et al., 2013). The mass concentration of $PM_{2.5}$ measured by the TEOM 1405 Monitor was suspected to be largely underestimated because the volatile even semi-volatile component in $PM_{2.5}$ can be easily lost at 50 ℃ which is designed in the TEOM 1405 Monitor for avoiding water condensation on the filter (Grover et al., 2005;Liu et al., 2014), e.g., under clean days after serious pollution episodes, the mass concentration of WSIs was even higher than the mass concentration of $PM_{2.5}$ measured by the TEOM 1405 Monitor (Fig. 1a). To verify above assumption, the concentrations of WSIs on the filters collected by the filter sampling method and the TEOM 1405 Monitor were comparatively measured, and the results are illustrated

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in Fig. 1c and Fig. 1d. It is evident that the proportions of NH_4^+, NO_3^- and Cl^- on the filter collected by the TEOM 1405 Monitor were dramatically lower than those on the filter collected by the filter sampling method, whereas SO_4^{2-} was on the contrary. It is well documented that temperature is a key factor affecting the distribution of both NH_4NO_3 and NH_4Cl on particle phase due to their thermo decomposition, e.g., at temperature greater than 35 ℃, little NH_4NO_3 is expected under typical ambient conditions (Finlayson-Pitts et al., 1986). The negative $PM_{2.5}$ values of the TEOM 1405 Monitor after a serious pollution episode also indicated the serious loss of the volatile component. Although the TEOM 1405 Monitor is widely used for measuring atmospheric $PM_{2.5}$ in the net stations of China, the pollution levels measured could only represent the lower limits, especially under the clean days after serious pollution episodes in winter.

3.2. Daily variations of WSIs in each season

The daily variations of WSIs in each season are illustrated in Fig. 2 and the statistic mass concentrations of the WSIs are summarized in Table 1. It is evident that the daily variations of the WSIs exhibited significantly periodic fluctuation, indicating meteorological conditions played a pivotal role in accumulation and dissipation of atmospheric pollutants. For example, the most frequently high pollution levels of the WSIs in winter were mainly ascribed to the relatively stable meteorological conditions with the low height of boundary layer which favors pollutants accumulation (Wang et al., 2013;Quan et al., 2014;Tian et al., 2014;Wang et al., 2014;Zhang et al., 2015a). Besides meteorological conditions, the extremely high levels of the WSIs during the pollution episodes revealed strong sources of the pollutants around Beijing.

The mean concentrations (μg m^{-3}) of WSIs 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

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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 Sect. 3.3) 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 Sect. 3.3), 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. 3.3).

3.3. The possible sources for the WSIs

To disclose the contribution of possible sources to the WSIs, the molar composition of the WSIs, the seasonal variation characteristics of typical WSIs, the variation characteristics of the three principal ions during serious pollution episodes, the contribution of secondary formation to atmospheric WSIs, and backward trajectories of air parcels were comprehensively analyzed.

3.3.1. The molar composition of the WSIs

The molar composition of water-soluble ions in each season under three pollution levels is illustrated in Fig. 3. With increasing pollution levels, the noticeable reduction of the proportions of metallic

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ions (such as Ca^{2+}, Na^{+} and Mg^{2+}) and the evident increase of NH_4^{+}, NO_3^{-} and SO_4^{2-} proportions revealed that the three principle ions (NH_4^{+}, NO_3^{-} and SO_4^{2-}) were mainly from atmospheric secondary formation. Compared with SO_4^{2-}, the fast increase of NO_3^{-} proportion with increasing pollution levels indicated that the formation rate of nitrate was faster than that of sulfate under higher pollution levels. It should be mentioned that the increase rate of NO_3^{-} proportion with increasing pollution levels was much slower in summer than in other seasons, validating that nitrate was easily thermal decomposed under high temperature. The conspicuous reduction of Cl^{-} proportion with increasing pollution levels meant Cl^{-} might be mainly from primary sources.

3.3.2. The seasonal variation characteristics of typical WSIs

The seasonal variation characteristics of typical WSIs are illustrated in Fig. 4. For Cl^{-} and K^{+}, their high concentrations mainly occurred in winter and autumn. It should be mentioned that the extremely high concentration of K^{+} in winter on 1 February (Fig. 2) was due to firework for celebrating Chinese lunar year (Jiang et al., 2015;Kong et al., 2015). Sea-salt has long been considered as the source for atmospheric Cl^{-} (Souza et al., 2014), however, the molar ratio of Cl^{-} to Na^{+} measured by this study (Fig. 5) in each season was above 1.30 which was much greater than the value of 1.18 in fresh sea-salt particles (Brewer, 1975), indicating sources other than sea-salt dominated atmospheric Cl^{-} in Beijing. Because K^{+} has been widely used as an indicator for biomass burning (Gao et al., 2011) and crop straw burning by stealth was prevailing in the countryside around Beijing during autumn and winter seasons, crop straw burning was suspected to be a common source for K^{+} and Cl^{-} (Li et al., 2014). The pronounced correlation coefficients ($r > 0.6$, $p < 0.01$) between K^{+} and Cl^{-} in the two seasons might be the circumstantial evidence for above suspicion. Several studies have reported extremely high emission factors of Cl^{-} (80-300mg Cl^{-}/kg coal) from the coal

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combustion in China (Huang et al., 2014). Because large fraction of coal consumed by farmers for heating in winter was the extra source for atmospheric pollutants in the vast area of North China, the obviously higher Cl^- concentrations measured in winter than in other seasons (Fig. 2) indicated that coal combustion by farmers in winter might make great contribution to atmospheric Cl^- in Beijing. The source of atmospheric NO_x in Beijing is dominated by vehicles and relatively stable in the four seasons, and hence the ratios of Cl^- to NO_x can largely counteract the influence of accumulation and dispersion due to variation of meteorological factors for identifying the possible extra source of Cl^-. The ratio of Cl^- to NO_x in winter was about a factor of 2 greater than those in other seasons (Fig. 5), confirming that coal combustion by farmers in winter indeed made evident contribution to atmospheric Cl^- in Beijing. Previous field investigations in different areas of Chinese mainland also found relatively high Cl^- concentration in winter, which was also ascribed to coal combustion (Yu et al., 2013;Wu et al., 2014). In addition, fertilization events in the agricultural fields around Beijing might also make contribution to atmospheric Cl^-, because the volatile ammonium chloride is a kind of prevailingly used fertilizer in the NCP, e.g., the extremely high ratios of Cl^- to Na^+ (Fig. 5) were coincident with the cultivation seasons of spring and summer.

For Ca^{2+}, remarkably high concentrations occurred in both spring and autumn. 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 three serious pollution events with remarkable elevation of Ca^{2+} (Fig. 2) were coincident with the intensive harvest of maize and tillage of the agricultural fields for planting winter wheat in the countryside around Beijing, and hence the extremely high Ca^{2+} concentrations in autumn were suspected to be from the farmers' activities. Because abundant

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234 atmospheric mineral particles were absorbed by crop leaves during crop growing season, especially
235 in the North China where atmospheric mineral dust is always at high level (Zhang et al., 2013;Zhao
236 et al., 2013b), a large fraction of the mineral dust absorbed on the leaves of crop would be released
237 into the atmosphere during harvest with crop straw being crushed into pieces for returning to fields
238 which is a prevailing cultivation manner under the advocacy of governments for reducing the
239 influence of crop straw burning on the air quality.
240 For NH_4^+, SO_4^{2-} and NO_3^-, remarkably high concentrations also appeared in both winter and autumn.
241 NH_4^+ was mainly from the reactions of NH_3 with acid gases (such as HNO_3) and acid particles, and
242 hence its variation trend was the same as those of SO_4^{2-} and NO_3^-. Although atmospheric NH_3 has
243 long been considered to be mainly from agricultural activities, their emissions mainly focus on
244 warmer seasons (Krupa, 2003). However, the frequently high concentrations of NH_4^+ appeared in
245 winter. Beside the slow thermal decomposition of ammonium nitrate, strong NH_3 emission sources
246 other than agricultural activities were suspected to be responsible for the frequently high
247 concentrations of NH_4^+ in the cold winter. Emissions of NH_3 from vehicles was regarded as an
248 important source (Liu et al., 2014). In addition, strong emission of NH_3 from domestic coal stoves
249 was indeed found by our preliminary measurements (data were not shown). During the serious
250 pollution episodes, the concentrations of SO_2 in autumn were almost the same as those in summer
251 and about one magnitude lower than in winter (Fig. 6), but the peak concentrations of SO_4^{2-} in
252 autumn were about two times greater than those in summer and at almost the same level as those in
253 winter. The gaseous phase reaction with OH (Zhao et al., 2013c;Quan et al., 2014), the
254 heterogeneous reaction on mineral dust (He et al., 2014;Nie et al., 2014), and multiphase reactions
255 in the water of particulate matters (Zheng et al., 2015a) of SO_2 have been recognized to be

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256 responsible for atmospheric SO_4^{2-} formation. The significant elevation of both Ca^{2+} and SO_4^{2-} in
257 autumn implied that the heterogeneous reaction of SO_2 on the mineral dust might greatly accelerate
258 the conversion of SO_2 to SO_4^{2-}. Although evidently high concentrations of Ca^{2+} occurred (Fig. 2 and
259 Fig. 4) in spring and SO_2 concentrations were much greater in spring than in autumn (Fig. 6), the
260 SO_4^{2-} concentrations were about a factor of 2 less in spring than in autumn. Atmospheric humidity
261 was suspected to play an important role in the heterogeneous reaction, e.g., the relative humidity
262 was much higher in autumn than in spring during the serious pollution events (Fig. 6). Similar to
263 SO_4^{2-}, the relatively high concentrations of NO_3^- during the serious pollution events in autumn were
264 also ascribed to the heterogeneous reaction of NO_2 on the mineral dust.

265 3.3.3. The variation characteristics of the three principal ions during serious pollution episodes

266 As shown in Fig. 6, the serious pollution episodes with noticeable elevation of various pollutants
267 usually occurred under slow wind speed (less than 2 m s^{-1}) and high relative humidity. In comparison
268 with their precursors of SO_2 and NO_x, however the detailed variation trends of SO_4^{2-} and NO_3^- were
269 different, indicating that the elevation of SO_4^{2-} and NO_3^- was not simply ascribed to the physical
270 process of accumulation. It is interesting to be noted that the increasing rates of SO_4^{2-} during some
271 serious pollution events especially with elevation of Ca^{2+} (such as in spring and autumn) were much
272 slower than those of NO_3^-, implying that the atmospheric heterogeneous reaction of NO_2 on the
273 mineral dust might be faster than that of SO_2. In comparison with summer and winter, the relatively
274 high ratios of NO_3^-/SO_4^{2-} in spring and autumn (Fig. 5) also supported above assumption.

275 3.3.4. Secondary formation for atmospheric sulfate and nitrate

276 The nitrogen oxidation ratio NOR = $nNO_3^- / (nNO_3^- + nNO_x)$ (n refers to molar concentration) and
277 the sulfur oxidation ratio SOR = $nSO_4^{2-} / (nSO_4^{2-} + nSO_2)$ have been used to estimate the degree of

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278 secondary formation of NO_3^- and SO_4^{2-}, which can counteract the interference of meteorological
279 factors (Chan and Yao, 2008;Yu et al., 2013;Guo et al., 2014;Huang et al., 2014;Yang et al.,
280 2015b;Zheng et al., 2015b). The values of NOR and SOR during haze days and non-haze days in
281 four seasons are listed in Table 2. Both the values of NOR and SOR on non-haze days were found
282 to be the highest in summer and the lowest in winter, well reflecting the seasonal variation of
283 photochemical intensity. Although sunlight intensity greatly reduced at ground level during haze
284 days, the values of NOR and SOR were about a factor of 2 greater during haze days than during
285 non-haze days in the four seasons, implying again that the heterogeneous or multiphase reactions of
286 SO_2 and NO_2 on atmospheric particles made significant contribution to atmospheric sulfate and
287 nitrate.

288 3.3.5. The influence of air mass transport on the WSIs in Beijing

289 To reveal the air mass transport influence on the WSIs in Beijing, three-day backward trajectories
290 for clusters and the corresponding mass concentrations of WSIs in each season were analyzed, and
291 the results are illustrated in Fig. 7. It could be seen that the lowest concentrations of WSIs usually
292 occurred in the northwest/northeast airflow with long distance transport. Because Beijing is
293 surrounded by mountains in the north/northwest/northeast directions where the population is sparse,
294 these clusters brought the relatively clean air mass to accelerate the dissipation of aerosols. The
295 highest concentrations of WSIs (especially for SO_4^{2-}, NO_3^- and NH_4^+) were usually observed in the
296 air parcel from southwest/south regions with high density of population. Considering the large
297 fraction (~30%) of air parcel from the southwest/south regions in each season, the human activities
298 in the southwest/south regions made evident contribution to the atmospheric WSIs in Beijing.
299 Besides the industries, the emissions from the high density of farmers in the southwest/south regions

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of Beijing was also suspected to make evident contribution to the atmospheric WSIs in Beijing, e.g., the remarkable elevations of Cl^- in winter and Ca^{2+} in autumn were probably from farmers' coal combustion for heating and harvest of maize, respectively.

3.4. 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 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 mass concentration ratios of NO_3^-/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 favored 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 significant contribution to atmospheric nitrate.

4. Conclusions

The comparison between the mass concentrations of WSIs measured by the filter method and the mass concentrations of $PM_{2.5}$ measured by the TEOM 1405 Monitor revealed that the mass concentrations of WSIs could well reflect the pollution status of $PM_{2.5}$ and the mass concentrations

of $PM_{2.5}$ measured by the TEOM 1405 Monitor were evidently underestimated due to the serious loss of volatile components in the atmospheric particulate matters.

The conspicuous 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 strongly periodic activities of farmers, such as crop harvest, crop straw burning, and coal combustion for heating, were found to make evident contribution 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 aroused great 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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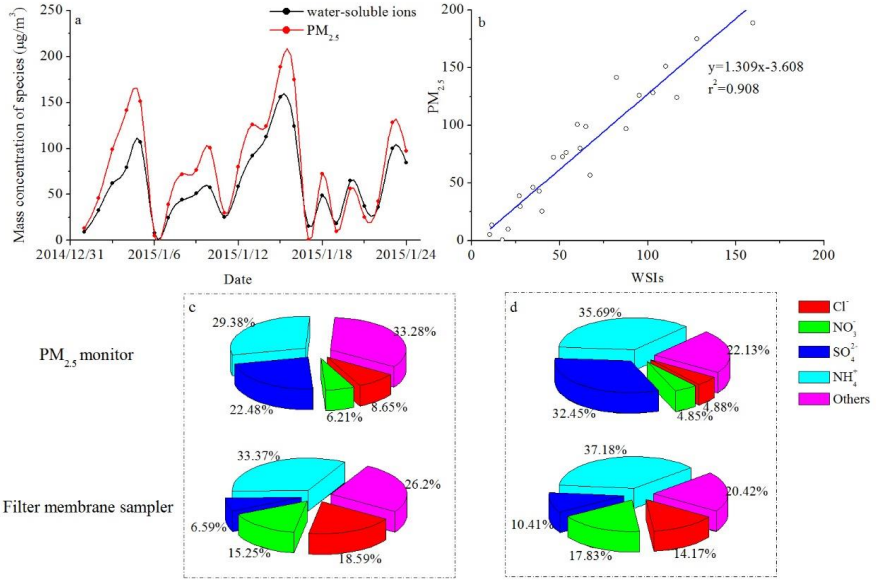

Fig. 1 Comparison between the filter sampling method and the $PM_{2.5}$ monitor for the daily average mass concentrations of the WSIs and $PM_{2.5}$ (Fig. 1a and 1b), and for the 12-day-average molar composition of the WSIs on the filters collected by the two methods during the two 12-day sampling periods (Fig. 1c represents the data collected during the first 12-day; Fig. 1d represents the data collected during the second 12-day.).

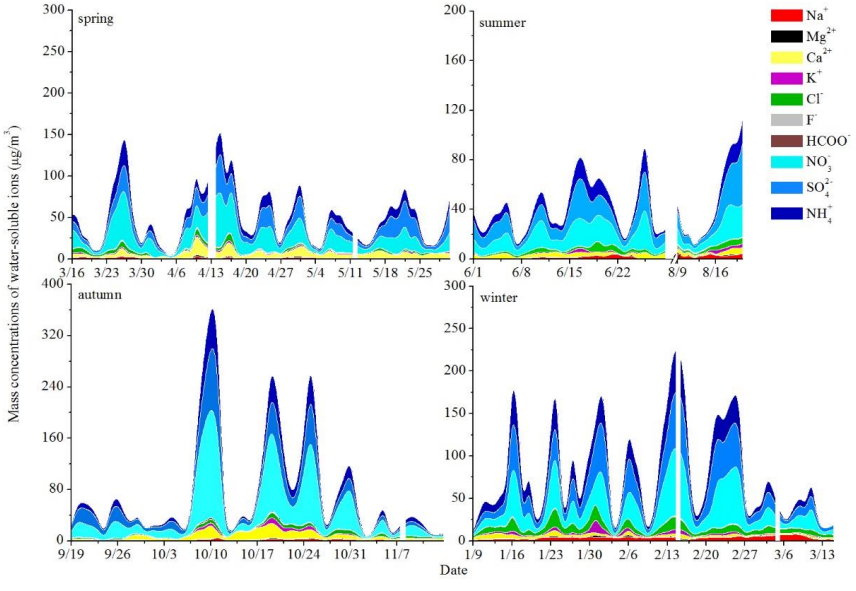

Fig. 2 Daily variations of WSIs in each season (the smooth lines for the WSIs were drawn between the points of the daily data).

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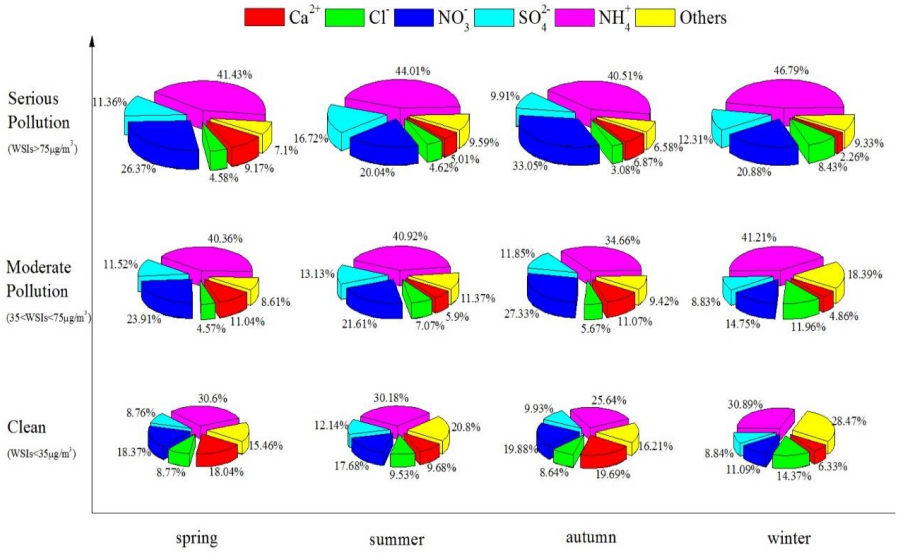

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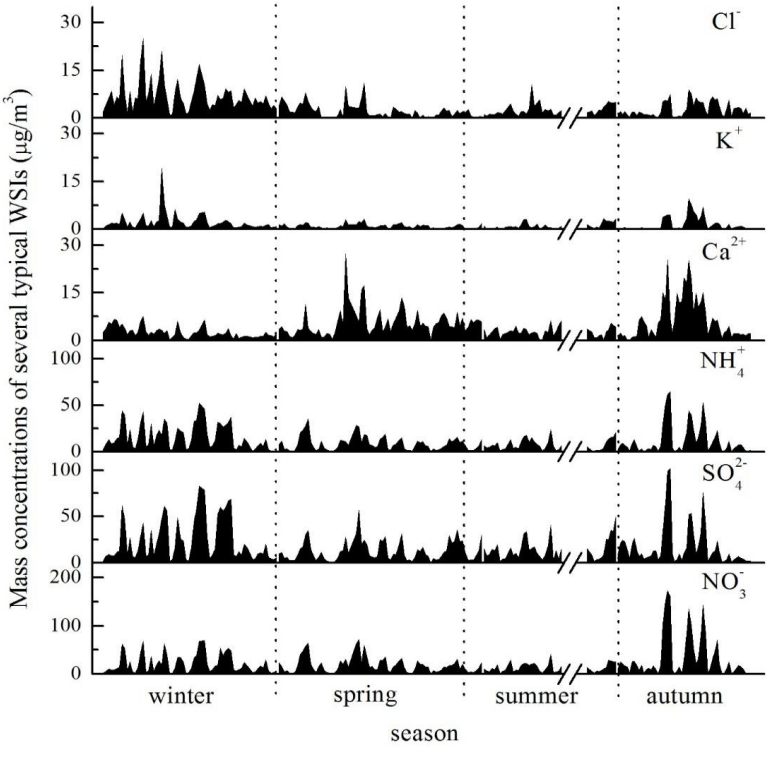
555 **Fig. 3** Molar composition of the WSIs under different pollution levels in four seasons (Clean: WSIs < 35μg m^{-3};
556 Moderate pollution: 35μg m^{-3} < WSIs < 75μg m^{-3}; Serious pollution: WSIs > 75μg m^{-3})



557
558 **Fig. 4** The seasonal variations of the several typical WSIs in the year of 2014

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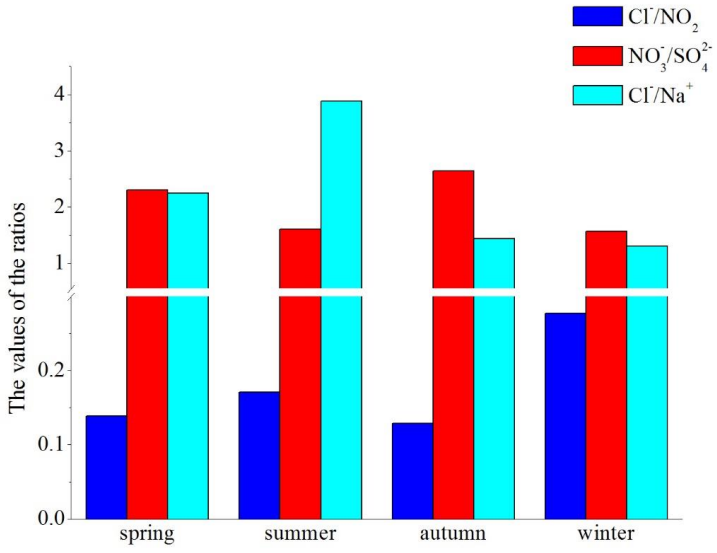

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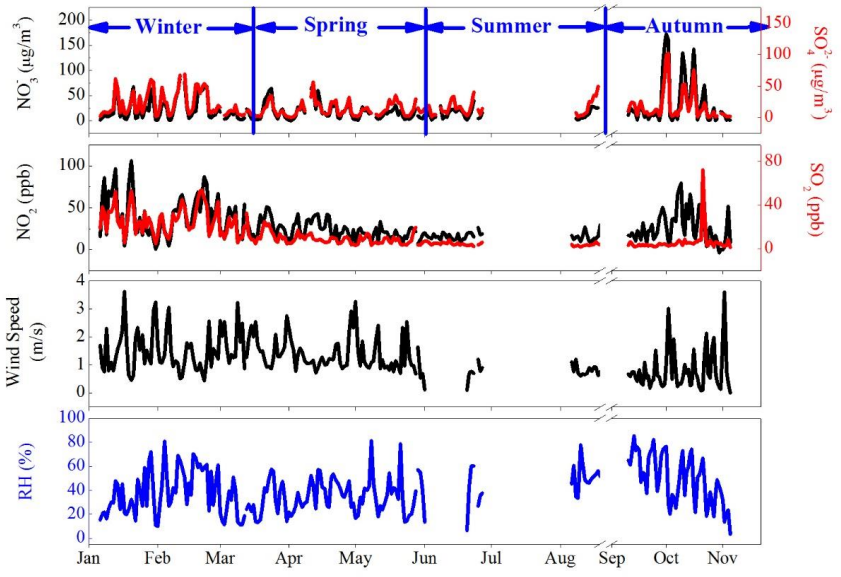
560 **Fig. 5** the average ratio of Cl^- /NO_2 (the unit is μg/m^3 and ppb, respectively) and the average molar ratios of Cl^-
561 /Na^+ and NO_3^-/SO_4^{2-} in each season.



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563 **Fig. 6** Time series of NO_3^-, SO_4^{2-}, NO_2 and SO_2 and meteorological data (wind speed and relative humidity) in four
564 seasons for 2014
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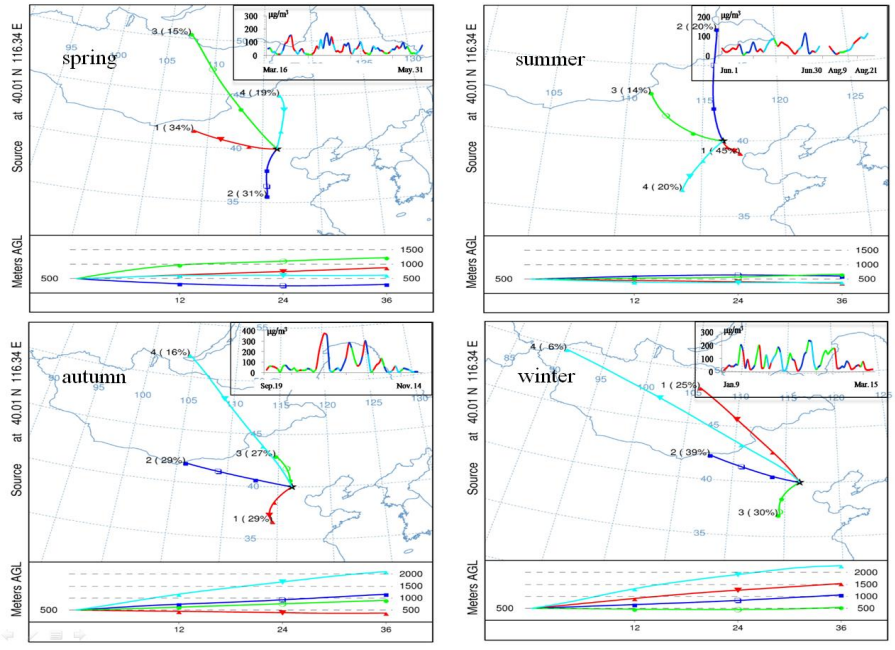

Fig. 7 The back trajectory cluster analysis and the corresponding overall ion mass concentration in four seasons

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

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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577 **Table 2** SOR and NOR during haze days and non-haze days in four seasons.

	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

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

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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 in Beijing.

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