A point-by-point response to the reviews

Thank you for your valuable comments. The followings are our responses to your comments.

Response to Reviewer #2

Comment 1: In this study Liu et al. characterized the water-soluble ions (WSIs) of $PM_{2.5}$ in Beijing on the basis of one-year filter sampling. This kind of intensive field and lab experiment is laborious. However, the authors fail to provide new findings and/or sound conclusion that can advance our understanding of haze pollution in Beijing, compared with previous dozens of publications. Most of important, solid evidence is critically needed to support their statement regarding the possible sources from agricultural activities.

Answer: Thank you for your valuable comments. To support our statements, the typical WSIs (Cl^-, Ca^{2+} and K^+) from a rural site (Fig. R1) are also presented in Fig. R2 to reveal the impact of periodic activities of farmers on the atmospheric WSIs. The rural site is far away from cities and industries, and thus the variation characteristics of atmospheric WSIs in the rural site are mainly affected by periodic farmers' activities and meteorological factors. Compared with the sampling site in Beijing city where coal has been almost replaced with natural gas and electricity for heating before 2013 (http://www.radiotj.com/gnwyw/system/2014/07/22/000485853.shtml), the extremely high concentrations of Cl^- in the rural site in winter indicated residential coal combustion for heating made evident contribution to atmospheric Cl^-; the obviously high concentrations of Cl^- in the rural site during the basal fertilization period for maize in June implied that volatilization of the prevailing NH_4Cl fertilizer under high temperature was an important source for atmospheric Cl^-; the relatively high concentrations of Ca^{2+} in June and October were ascribed to wheat harvest and maize harvest followed by soil ploughing, respectively; the obvious elevation of K^+, Cl^- and Ca^{2+} in the rural site in November when straw burning was prevailing in the region demonstrated their strong emissions from straw burning. To recognize the impact of the periodic emissions from farmers' activities on atmospheric WSIs in Beijing, the molar proportions of atmospheric WSIs in Beijing were comparatively analyzed before, during and after the periods of heating in winter, maize fertilization in summer, and maize harvest and soil ploughing in autumn (Fig. R3). Because the atmospheric Cl^- sources from sea-salt, industries, power plants and biofuels are relatively stable during the whole year and the average mass Cl^-/K^+ ratio of 7.1 (except for firework event during the Spring Festival) in winter was about a factor of 2 greater than the value of 3.8 in autumn when straw burning was prevailing in the region, the obvious elevation of Cl^- proportion (Fig. R3) as well as Cl^- concentrations (Fig. R2) in winter should be ascribed to the additional source of residential coal combustion. Besides Cl^-, the serious emissions of various pollutants from residential coal combustion (Zhang and Tao, 2008; Zhang et al., 2008; Li et al., 2016) must make evident contribution to deteriorate the air quality in Beijing during the wintertime. Compared with the periods before and after maize fertilization, the proportion of Cl^- during maize fertilization in summer increased about 3%-4%, confirming the influence of maize fertilization on atmospheric Cl^- in Beijing. Because fertilization is an important source for atmospheric NH_3, the elevation of Cl^- (as a tracer for fertilization) revealed that fertilization in the rural areas around Beijing could also make obvious contribution to atmospheric NH_4^+ in Beijing. The remarkable elevation of Ca^{2+} proportion in Beijing during the period of the maize harvest and

soil ploughing provided convincing evidences that the agricultural activities indeed influenced on atmospheric Ca^{2+} in Beijing. The above discussion has been added in our revised manuscript.

Comment 2: In addition, the concentrations of WSIs are so high that close to $PM_{2.5}$ (e.g., Figure 1), arising the concern of the data quality. In general, organics are equally as important as WSIs in $PM_{2.5}$, especially during days with lower $PM_{2.5}$. If possible, the authors should perform mass closure studies to ensure the data quality.

Answer: The comparison between the WSIs and $PM_{2.5}$ measured by the TEOM monitor is far from the topic of the manuscript, and hence this part has been delated in our revised manuscript. According to your valuable suggestions, we will perform mass closure studies in the near future.

Comment 3: Detailed evidence to support the points is critically needed. For example: (a) Line 15: Farmers' activities; (b) Line 17: fertilization of NH_4Cl; (c) Line 18: Cl^- from coal combustion by farmers.

Answer: The evident elevation of Cl^- and K^+ in Beijing during the autumn indicated biomass burning, one of the farmers' activities, was an important source for atmospheric WSIs, which was in good agreement with previous studies (Wang et al., 2005; Souza et al., 2014; Yang et al., 2016). The proportion of Cl^- was much higher during basal fertilization for maize in summer than before and after the fertilization event (Fig. R3) and the extremely high ratio of Cl^- to Na^+ in summer among the four seasons well revealed the contribution of volatilization of the prevailing NH_4Cl fertilizer (Ishikawa et al., 2015). The distinct seasonal variation of Cl^- (Fig. R2), the proportion of Cl^- in WSIs (Fig. R3) and the ratio of Cl^- to K^+ could reflect the contribution of coal combustion by farmers to atmospheric Cl^-.

Comment 4: Line 18: Biomass/biofuel burning also contributes to Cl^- emissions in winter?

Answer: Yes, biomass and biofuel burning could also contribute to Cl^- emissions in winter (Christian et al., 2010; Li et al., 2014). However, the emission of biofuel burning is relatively stable during the whole year and the average mass Cl^-/K^+ ratio of 7.1 (except for firework event during the Spring Festival) in winter was about a factor of 2 greater than the value of 3.8 in autumn when biomass (straw) burning was prevailing in the region. Therefore, the obvious elevation of Cl^- proportion in WSIs as well as the extremely high Cl^- concentrations in winter should be ascribed to the additional source of residential coal combustion.

Comment 5: Line 19: Mineral dust, including Ca^{2+}, was transported from farmland to urban region? Construction activities also contributed to high values of Ca^{2+} in urban region.

Answer: Yes, construction activities are an important source for atmospheric Ca^{2+} in urban region. However, there are few construction activities in the rural area, which couldn't explain the extremely high concentrations of Ca^{2+} over there during the autumn (Fig. R2). The extremely high concentrations of Ca^{2+} in Beijing occurred during the period of 6-25 October when the air parcels were mainly from the southwest/south regions (Fig. R4) where the vast areas of agricultural field

were under intensive maize harvest and soil ploughing. Although the concentrations of Ca^{2+} in the rural area were still kept high levels during the period of 2-14 November (Fig. R2), 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. R4) where agricultural activities are relatively sparse. Considering the relatively stable contribution of construction activities to mineral dust during each season (Zhu et al., 2005), the coincident elevation of Ca^{2+} in both the rural and urban areas and the evident increase of Ca^{2+} proportion in WSIs of Beijing during the period of 6-25 October (Fig. R2 and Fig. R3) revealed the influence of the maize harvest and soil ploughing in the rural area on atmospheric Ca^{2+} in Beijing.

Comment 6: Line 27, Note that industrial emissions from south regions in NCP are also massive.

Answer: There are massive industrial emissions from south regions in NCP. However, the emission of industries is relatively stable during the whole year (Gao et al., 2014), which cannot explain the distinct variations of the molar proportions of atmospheric WSIs in Beijing before, during and after the periods of heating in winter, maize fertilization in summer, and maize harvest and soil ploughing in autumn.

Comment 7: Line 36: $PM_{2.5}$ is not defined due to haze. The terminology should be clarified.

Answer: The mistake has been corrected in our revised manuscript: "The severe haze pollution is mainly ascribed to elevation of fine particulate matter with dynamic diameter less than 2.5μm ($PM_{2.5}$)".

Comment 8: Line 47-48: The authors should specify what traffic emissions included here, particles, gas, or both? Is it true that 4% of $PM_{2.5}$ was attributed to vehicle exhaust from Huang et al., 2014? This may be a wrong citation.

Answer: According to your valuable comments, we specify the traffic emissions. The traffic emissions reported in these references only included particles. Sorry, the reference should be Zhang et al., 2013. The mistakes have been corrected in our revised manuscript.

Comment 9: Line 55: How does this work advance our knowledge?

Answer: According to your valuable comments, the seasonal variation characteristics of WSIs in a rural site (Baoding, Hebei Province) have been added in our revised manuscript to advance our knowledge about the emissions from farmers' activities. Farmers' activities were found to make evident contribution to atmospheric WSIs in Beijing, based on the investigations about the seasonal variation characteristics of WSIs in both the rural and urban areas, and the distinct variations of the molar proportions of atmospheric WSIs in Beijing before, during and after the periods of heating in winter, maize fertilization in summer, and maize harvest and soil ploughing in autumn.

Comment 10: Line 65: totally?

Answer: "Totally" has been replaced with "mostly".

Comment 11: Line 73: What is the size of the particle on the crop leaves? More information is needed to show how long it can be transported. Also, wind speed is a key factor here.

Answer: The size of the particle on the crop leaves was not measured in this study. The previous studies confirmed that various plants can absorb atmospheric $PM_{2.5}$ and PM_{10} (Bealey et al., 2007; Ji et al., 2013). There are about 300,000 km^2 agricultural fields where the harvest of wheat or maize mainly concentrates about two weeks in the NCP, and hence the emissions of mineral dust are suspected to be massive during the harvest through the harvest scene (Fig. R5). Although we don't know how long the particle from the harvest can be transported, the remarkable elevation of Ca^{2+} proportion in Beijing during the period of the maize harvest and soil ploughing provided convincing evidences that the agricultural activities indeed influenced on atmospheric Ca^{2+} in Beijing. Both wind speed and wind direction are indeed key factors for the transportation, while back trajectory is widely used for recognizing the transportation of pollutants. The extremely high concentrations of Ca^{2+} in Beijing occurred during the period of 6-25 October when the air parcels were mainly from the southwest/south regions (Fig. R4) where the vast areas of agricultural field were under intensive maize harvest and soil ploughing. Although the concentrations of Ca^{2+} in the rural area were still kept high levels during the period of 2-14 November (Fig. R2), 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. R4) where agricultural activities are relatively sparse. According to your valuable comments, we will perform the study about the size of the particle on the crop leaves in the near future.

Comment 12: Line 80: The authors should provide more solid evidence to show farmers' influences on an urban site in BJ?
Line 229-233: Again, more direct evidences are needed, if the authors wish to link the Ca^{2+} in urban site to farmland.
Line 213-215: Detail explanation was needed here, how can the authors identify that coal combustion by farmers in winter might make great contribution to atmospheric Cl^- other than coal combustion from urban area?

Answer: Solid evidence has been added in our revised manuscript (See the answers for comments 1, 3, 4 and 5).

Comment 13: Line 84: Can the contribution be quantified in this study?

Answer: It is difficult to quantify the contribution in this study because of the complex sources of atmospheric WSIs as well as the impact of meteorological factors. We are conducting the emission factors of various pollutants from typical farmers' activities such as residential coal combustion, the NH_3 emissions of agricultural field and so on, which will be helpful to quantify the contribution in the near future.

Comment 14: Line 91: Is this kind of filter suitable for the sampling at the site with high loading of $PM_{2.5}$?

Answer: The PTFE filter is widely used for PM sampling in previous studies (Chow et al., 1996; Walker et al., 2006; Pathak et al., 2009; Chen et al., 2015; Park et al., 2015). The significant correlation between WSIs sampled by the filters and $PM_{2.5}$ measured by the TEOM monitor (Fig. R6a), and the near equilibrium between cations and anions in the four seasons (Fig. R6b) indicated that this kind of filter is suitable for the sampling at the site with high loading of $PM_{2.5}$.

Comment 15: Line 93: Why started at 3 pm, background information is needed.
Line 99: How blank filters are sampled? It is better to show the blank values.

Answer: To conveniently replace the filter sample in each day, we select 3 p.m. as our starting time. Blank filters were brought to the field and were installed in the samplers which no air was pumped. After sampling, all the filters samples including blank filters were put in dedicated filter storage containers (90mm, Millipore) and preserved in a refrigerator till ion analysis. All the ion concentrations were corrected for blanks. The average blank values were about 0.03mg L^{-1} for Na^+, Ca^{2+}, F^-, NO_3^- and SO_4^{2-}, 0.02mg L^{-1} for NH_4^+ and Cl^-, 0.01mg L^{-1} for Mg^{2+}, K^+ and $HCOO^-$. According to your valuable comments, the blank values have been shown detailedly in our manuscript.

Comment 16: Line 114: How far is it from the observation site? Are the meteorological data and air pollutants similar at these two different sites?

Answer: There are about 20m between the observation station and our sampling site at almost the same height of 25m.

Comment 17: Line 116: Why 72h and 500m above sampling position were selected?

Answer: Due to the regional meteorological conditions with about 4-7 days periodic cycle (Guo et al., 2014), 72h is usually selected as the least elapsed time for recognizing regional transportation. Considering the surrounding terrain of Beijing and the height of planet boundary layer, air parcel with the height of 500m is recommended by NOAA for tracing their sources. In addition, the parameters have also been employed by previous studies (Li et al., 2012; Wang et al., 2015; Yang et al., 2016).

Comment 18: Line 128: Are there new findings by using this filter sampling method, compared with method described in section 2.1?
Line 135: How the mass of $PM_{2.5}$ filter was determined?
Line 140: Base on the comparison between filter sampling method and the TEOM 1405 Monitor, the authors can give out the underestimated percentage of concentrations of $PM_{2.5}$ and WSIs due to the volatile even semi-volatile component.
Line 154: This may be a good point to argue, but more details are needed.
Figure 1: The concentrations of WSIs are so high that close to $PM_{2.5}$. In general, organics are also

as equally important as WSIs in Beijing, especially during days with lower $PM_{2.5}$. Mass closure studies are needed to check the data quality.

Answer: As mentioned above, the comparison between the WSIs and $PM_{2.5}$ measured by the TEOM monitor is far from the topic of the manuscript, and hence this part has been delated in our revised manuscript.

Comment 19: Line 192: Why nitrate was faster than sulfate under higher pollution levels. Line 195: Please show the pattern in different seasons.

Answer: The faster increase of nitrate proportion than that of sulfate proportion from clean days to serious pollution days mainly occurred in spring and autumn when the concentration levels of Ca^{2+} were relatively high. To recognize the influence of Ca^{2+} concentrations on the formation of nitrate and sulfate, the formation rates of nitrate and sulfate were analyzed under typical cases of haze formation in the four seasons (Fig. R7). It is evident that the faster formation rates of nitrate than those of sulfate only occurred under the relatively high levels of Ca^{2+} in spring and autumn, indicating that the mineral dust could preferentially promote nitrate formation.

Comment 20: Line 217: Why the ratio Cl^- to NO_x was selected? They are different in phases in the atmosphere.

Answer: NO_x in Beijing is dominated by vehicles and relatively stable during the whole year. Although Cl^- and NO_x are different in phases in the atmosphere, the Cl^-/NO_x ratio value can counteract the influence of meteorological factors and reveal the additional sources for atmospheric Cl^- in the four seasons. Considering this situation, the Cl^-/NO_x ratio has been delated in our revised manuscript.

Comment 21: Line 248-249: This is an important point and the evidence is critically needed.

Answer: NH_3 emissions generated from a prevailing residential coal stove fueled with raw bituminous coal were investigated under alternation cycles of flaming and smoldering combustion in our preliminary studies. The NH_3 emission factor for the residential coal stove was recorded as 0.62-1.10g/kg coal, which was in line with Li et al., 2016. These results indicated that residential coal combustion may be a significant NH_3 emission source in the cold winter, and hence leading to the elevation of atmospheric NH_4^+ in Beijing.

Response to Reviewer #1

Comment 1: So many studies have already been carried out for the chemical compositions from $PM_{2.5}$ in Beijing. Because of the lack of other related aerosol measurements, this paper basically focuses on the simple display of the ion concentrations. Most of the discussion are based on speculation, and no new ideas and no interesting points are found in this paper. On the whole, this paper is not suitable for publication in the ACP.

Answer: According to your comments, the seasonal variation characteristics of WSIs in a rural site

(Baoding, Hebei Province) have been added in our revised manuscript to advance our knowledge about the emissions from farmers' activities. Farmers' activities were found to make evident contribution to atmospheric WSIs in Beijing, based on the investigations about the seasonal variation characteristics of WSIs in both the rural and urban areas, and the distinct variations of the molar proportions of atmospheric WSIs in Beijing before, during and after the periods of heating in winter, maize fertilization in summer, and maize harvest and soil ploughing in autumn.

Although we didn't conduct other related aerosol measurements, the variation characteristics of the composition of the water-soluble ions in $PM_{2.5}$ were found to well reflect their possible sources, and the following important conclusions were derived from the measurements: 1. Because the atmospheric Cl^- sources from sea-salt, industries, power plants and biofuels are relatively stable during the whole year and the average mass Cl^-/K^+ ratio of 7.1 (except for firework event during the Spring Festival) in winter was about a factor of 2 greater than the value of 3.8 in autumn when straw burning was prevailing in the region, the obvious elevation of Cl^- proportion (Fig. R3) as well as Cl^- concentrations (Fig. R2) in winter should be ascribed to the additional source of residential coal combustion. Besides Cl^-, the serious emissions of various pollutants from residential coal combustion (Zhang and Tao, 2008; Zhang et al., 2008; Li et al., 2016) must make evident contribution to deteriorate the air quality in Beijing during the wintertime. 2. Compared with the periods before and after maize fertilization, the proportion of Cl^- during maize fertilization in summer increased about 3%-4%, confirming the influence of maize fertilization on atmospheric Cl^- in Beijing. Because fertilization is an important source for atmospheric NH_3, the elevation of Cl^- (as a tracer for fertilization) revealed that fertilization in the rural areas around Beijing could also make obvious contribution to atmospheric NH_4^+ in Beijing. 3. The remarkable elevation of Ca^{2+} proportion in Beijing during the period of the maize harvest and soil ploughing provided convincing evidences that the agricultural activities indeed influenced on atmospheric Ca^{2+} in Beijing. With the elevation of Ca^{2+} in spring and autumn, the evidently faster increasing rates of NO_3^- than SO_4^{2-} implied that the atmospheric heterogeneous reaction of NO_2 on the mineral dust was an important source for NO_3^-. To our best knowledge, there are still no reports about the above conclusions which will be helpful for future control measures in reducing pollutant emissions from rural areas in the North China Plain. Additionally, the heterogeneous reaction of NO_2 on mineral dusts has been found to make contribution to nitrate formation under laboratory simulations, but the role of the reaction for nitrate formation has not been recognized in field measurements before this study. Because field measurement is one of the main subject areas of the ACP and there are original findings in the paper, we think the paper is suitable for publication in the ACP.

Comment 2: In addition, there are also some problems and mistakes in this paper. After major revision, this paper might be suitable for publication in some local journals. It is strongly recommended that this paper be send to a language editing service. There are too many Chinese English in this paper. For example, the use of the word "farmer" is inaccurate, even ridiculous, just as "with high density of famers", "farmers' activities", "heating by farmers". At present, most of the people living in the rural area are not engaged in agricultural activities. And farmers have also not engaged in agricultural activities in most of the time. You should use the "rural area" and "agricultural activities" to describe the exact meaning.

Answer: Thank you for your valuable comments. We have revised our manuscript and corrected

some mistakes in this paper. However, to our best knowledge, "farmer" is a commonly used word to represent for people who are living in rural areas (Xhoxhi et al., 2014; Pattey and Qiu, 2012; Rio et al., 2011; Mahmud, 2009) and the "rural area" was also used for representing the countryside in the text of the paper. In addition, the "farmers' activities" in this paper included both "agricultural activities" and farmers' living activities (cooking and heating via coal combustion, etc.), and hence "farmers' activities" is more exact than "agricultural activities" for describing our meanings.

Comment 3: Line 70, "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." This statement is basically impossible to be true. There is no evidence that the crop could absorb $PM_{2.5}$. And the smashing process of crop straw could not be an important source of $PM_{2.5}$. Just a small amount coarse PM might be emitted.

Answer: The previous studies have confirmed that various plants can absorb atmospheric $PM_{2.5}$ and PM_{10} (Bealey et al., 2007; Ji et al., 2013). There are about 300,000 km^2 agricultural fields where the harvest of wheat or maize mainly concentrates about two weeks in the NCP, and hence the emissions of mineral dust are suspected to be massive during the harvest through the harvest scene (Fig. R5). In addition, the remarkable elevation of Ca^{2+} proportion in Beijing during the period of the maize harvest and soil ploughing as well as the back trajectory cluster analysis (See the answers of comment 5 of Reviewer #2) provided convincing evidences that the agricultural activities indeed influenced on atmospheric Ca^{2+} in Beijing.

Comment 4: Line 74, what's the meaning of "pollutant emissions from the chimney of the farmers' coal stoves"? There is not a thing called "farmers' coal stoves" in this world. I think "pollutants from coal combustion for heating" is more accurate. The author is not familiar with the countryside.

Answer: Because "pollutants from coal combustion for heating" includes various sources from industrial boilers, central-heating boilers as well as residential coal stoves, this word might be difficult to describe the meaning of the sentence accurately. According to your suggestion, the revised manuscript has replaced "the farmers' coal stoves" with "the residential coal stoves". It should be mentioned that the corresponding author of this paper was born and grew up in a village of the North China Plain and frequently visits the village every year. In addition, our group has been engaged in field measurements of N_2O emissions for about ten years. Therefore, we are familiar with the rural areas very well.

Comment 5: Line 94, "dedicated filter storage containers"? I think it should be a desiccator.

Answer: The dedicated filter storage container is not a desiccator but a kind of dedicated box for storing the filters. The objective of this paper is to investigate the water-soluble ions in $PM_{2.5}$ not to measure the mass concentrations of $PM_{2.5}$, and hence desiccators were not used as containers for the filters. The dedicated filter storage containers are commercial products which have been widely used for storing the filters by investigators.

Comment 6: As mentioned in this paper, the TEOM 1405 is not suitable for accurate $PM_{2.5}$ mass concentration measurement owing to the volatilization of unstable components. Why didn't the authors weigh the PTFE filters before and after the sampling for mass concentration analysis? This is the biggest problem in this paper. The proportions of different ions in $PM_{2.5}$ could not be obtained.

Answer: In this paper, the variation characteristics of the water-soluble ions could provide the important information about the evident contribution of farmers' activities. The comparison between the WSIs and $PM_{2.5}$ measured by the TEOM monitor is far from the topic of the manuscript, and hence this part has been delated in our revised manuscript. According to your suggestions, we will perform mass closure studies in the near future.

Response to SC#1

Comment 1: The manuscript presents results from ion chromatography analysis of samples of $PM_{2.5}$ collected in Beijing through the year of 2014 aimed at deriving the variation characteristics of water-soluble ions (WSIs) in the $PM_{2.5}$. Since only a small part of studies focused on the variation characteristics of WSIs in the four seasons by now, I think the intentions of the authors are very good and substantial data about the WSIs in the $PM_{2.5}$ are provided which can make an incremental gain in the knowledge of the haze occurred in Beijing. The science is sound and the results are meaningful. In addition, the authors are very familiar with the North China plain (NCP) and the agriculture activities and living activities of farmers in NCP. There are interesting findings that the emissions from farmers' activities in the NCP was one possible emission sources and the influence of fertilization events and crop straw have influence on the regional air quality during the harvest seasons periods which have been neglected by most previous studies. Maybe more attention would be paid to the agriculture activities in NCP and that some field observations would be carried out in rural area after this paper. The detailed data of the daily variations of WSIs in this paper showed an obvious seasonal variation characteristic, which may helpful for further exploring how meteorological factor affect the accumulation and dispersion of atmospheric pollutants.

Answer: Thank you for your approval and your valuable comments. Just as you know, the corresponding author of this paper was born and grew up in a village of the North China Plain and frequently visits the village every year. In addition, our group has been engaged in field measurements of N_2O emissions for about ten years. Therefore, we are familiar with the rural areas very well. In recent years, our observation found that the frequent haze formation periods closely relate with the periodically strong emissions of pollutants from the rural area in the NCP, which mainly occurred in summer season of June-July during wheat harvesting period, autumn season of September-October during maize harvesting period and winter season during the heating period by residential coal combustion. Considering that the emissions from the rural area in the NCP are almost neglected, we presented the new ideas and the interesting points by tracing the sources of atmospheric WSIs in $PM_{2.5}$. The further exploring has been performed during the whole year 2015 and the contribution of periodic emissions from farmers' activities would be quantified in the near future.

Comment 2: And it was found that the atmospheric concentrations of SO_2 and NO_2 in autumn are much smaller than that in winter and spring, whereas the mean concentration of WSIs in autumn was almost the same as that in winter and nearly twice as that in spring. This result indicates that unknown mechanisms of atmospheric heterogeneous reactions and transformation of atmospheric pollutants from gas phase to particulate phase should be investigated. Moreover, it was an interesting observation that the increasing rates of SO_4^{2-} during some serious pollution events were much slower than those of NO_3^-, especially with the elevation of Ca^{2+}. The heterogeneous reactions of SO_2 and NO_2 with mineral dust may be an important pathway for the formation of sulfate and nitrate in the urban cities of East Asia because of the frequent occurrence of dust storms. Most previous studies focused on the heterogeneous uptake of SO_2 or NO_2 on mineral aerosol surfaces without considering coexistent gases in atmospheric condition. Only a few studies reported that SO_2 and NO_2 likely exert synergistic effect on the surface of mineral dust. To my knowledge there is still a lack of knowledge to explain why the increase of nitrate proportion with increasing pollution levels much faster than the increase of sulfate. I'm interested in the new ideas and inspiring points in this paper.

Answer: We entirely agree with your comments. The processes and evolution of haze pollution are characterized by the formation of substantial amounts of sulfate and nitrate (Sun et al., 2006; Zhao et al., 2013). The large amount of sulfate and nitrate were considered to be more likely generated via heterogeneous chemistry than gas-phase and aqueous-phase chemistry during haze days in China (Zhao et al., 2013; Wang et al., 2013). Modeling studies and laboratory simulations have researched on the role of heterogeneous reactions in sulfate and nitrate formation on the surface of mineral particles (Zheng et al., 2015), but the role of the reaction for nitrate formation has not been recognized in field measurements before this study.

The faster increase of nitrate proportion than that of sulfate proportion from clean days to serious pollution days mainly occurred in spring and autumn when the concentration levels of Ca^{2+} were relatively high. To recognize the influence of Ca^{2+} concentrations on the formation of nitrate and sulfate, the formation rates of nitrate and sulfate were analyzed under typical cases of haze formation in the four seasons (Fig. R7). It is evident that the faster formation rates of nitrate than those of sulfate only occurred under the relatively high levels of Ca^{2+} in spring and autumn, indicating that the mineral dust could preferentially promote nitrate formation. However, the reason might be further analyzed by laboratory simulation in the near future. Thank you.

References

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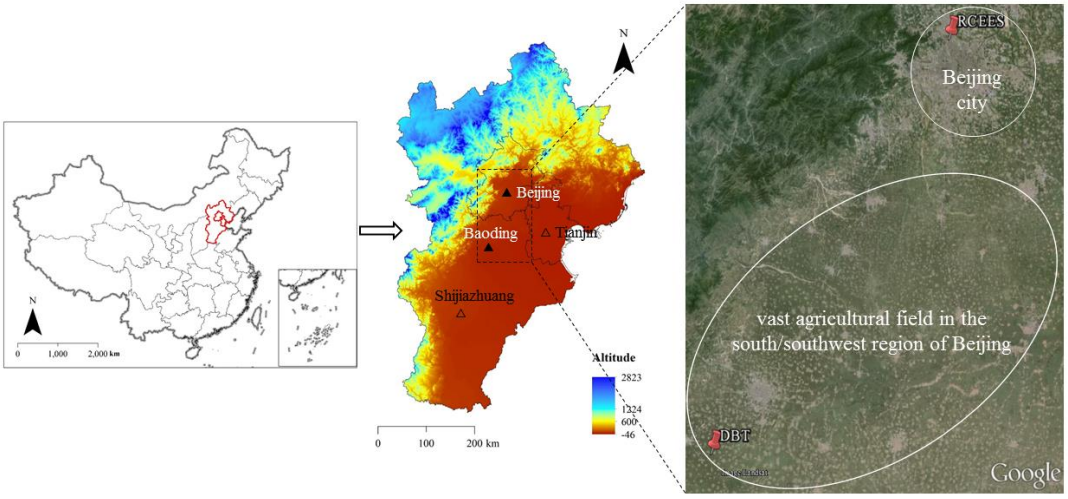
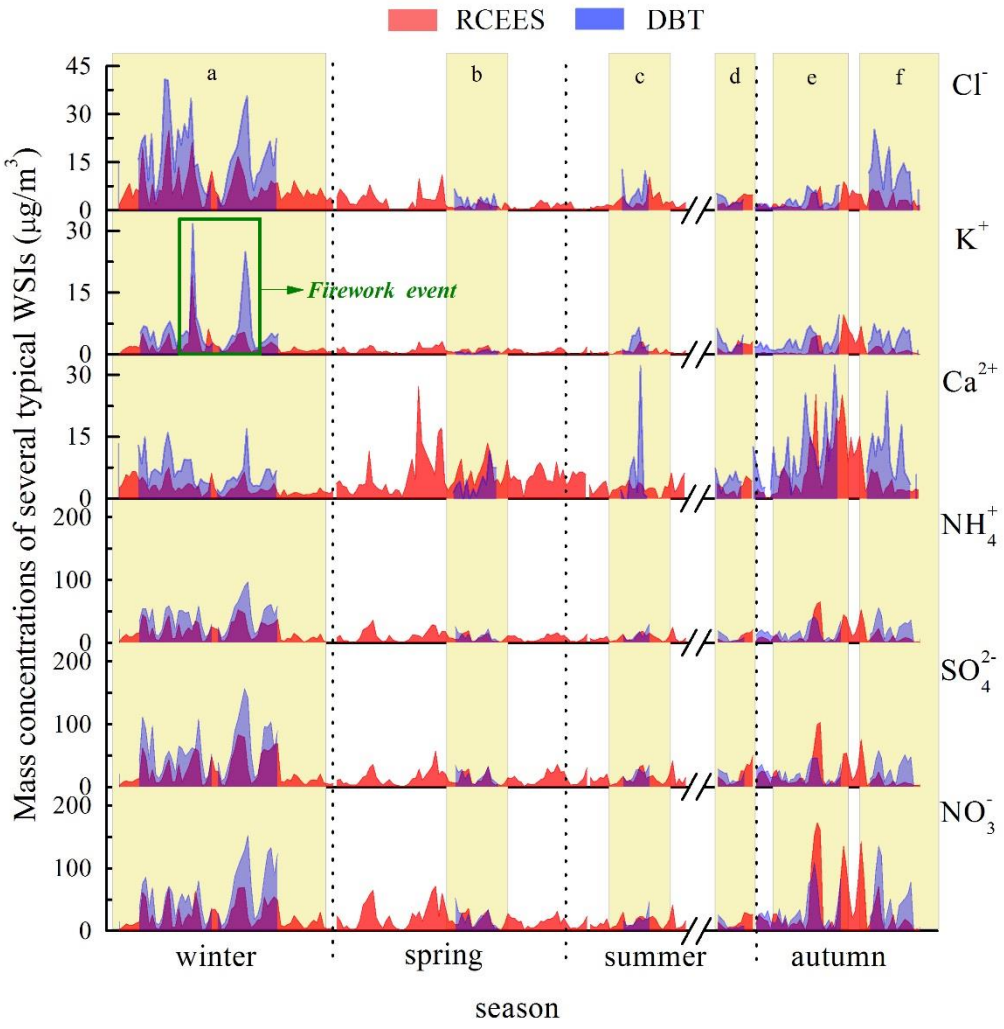


523

524 **Fig. R1** Sampling sites (the urban site in Beijing city and the rural site in Baoding, Hebei Province) in the NCP.



525

Fig. R2 Seasonal variations of the several typical WSIs in the year of 2014. (The mass concentrations of Cl^-, K^+, Ca^{2+}, NH_4^+, SO_4^{2-} and NO_3^- were presented at RCEES and DBT. The green square showed the firework event during the period of the Spring Festival. The gray square represented 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).)

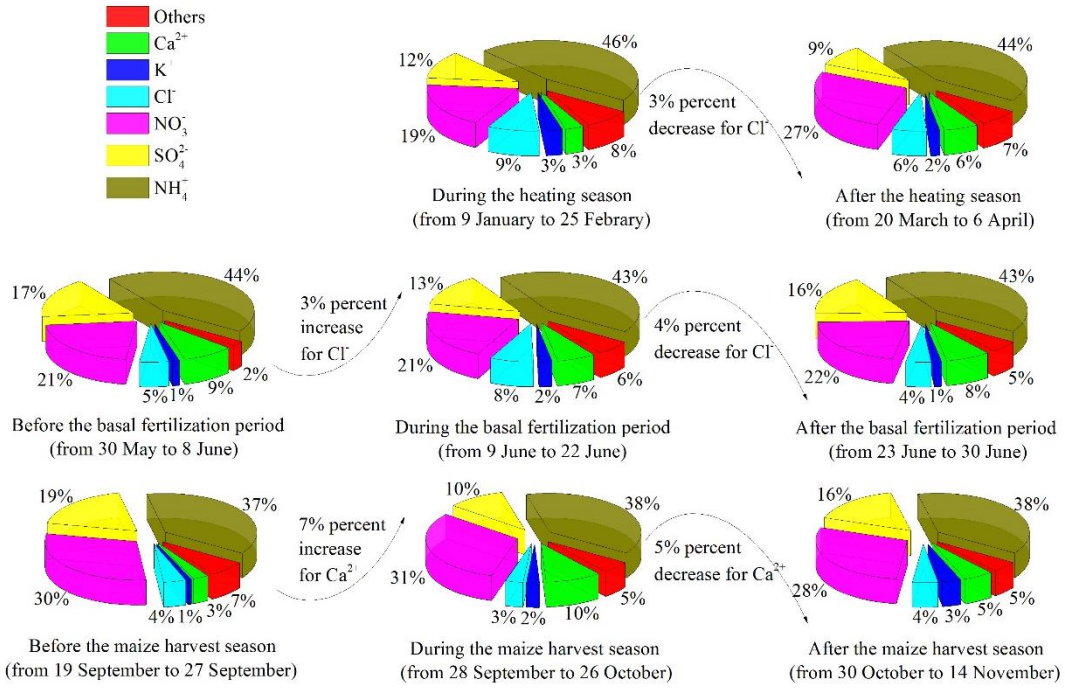


Fig. R3 Molar proportions of atmospheric WSIs in Beijing before, during and after the periods of heating in winter, maize fertilization in summer, and maize harvest and soil ploughing in autumn.

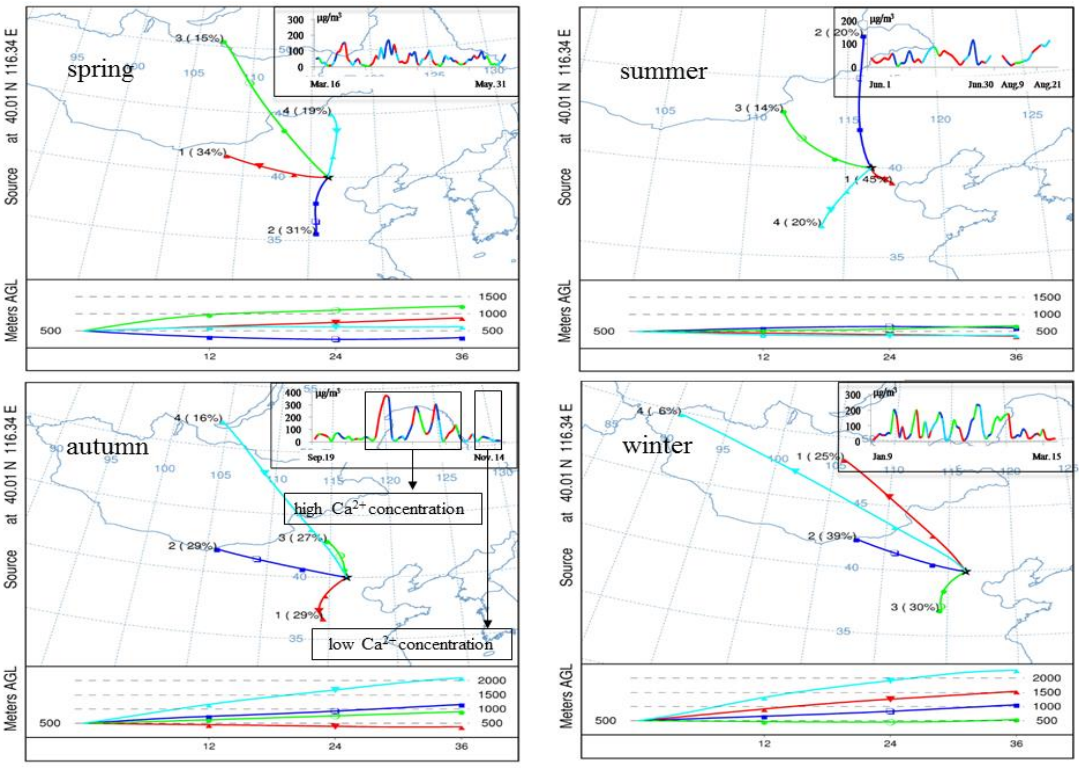


Fig. R4 The back trajectory cluster analysis and the corresponding overall ion mass concentration in four seasons.

Fig. R5 The harvest scene during the wheat harvest of 2014 in the rural area (close to our rural site) in Baoding, Hebei Province.

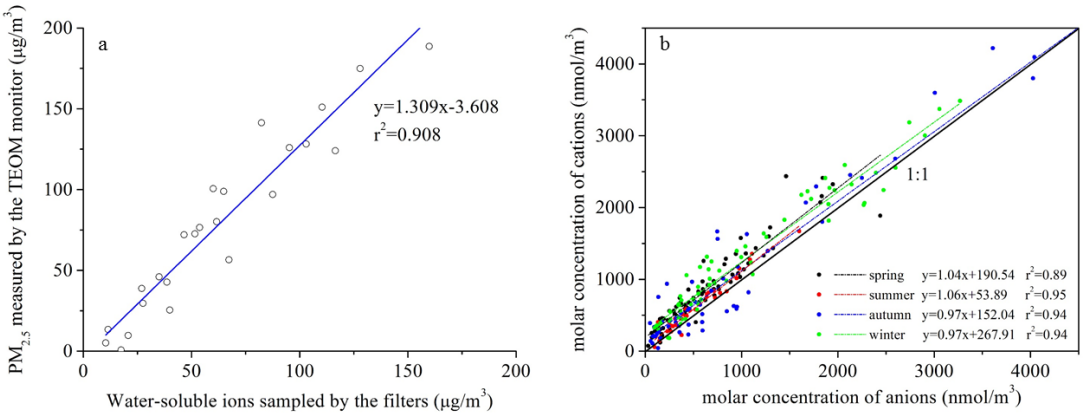


Fig. R6 The correlation between WSIs sampled by the filters and $PM_{2.5}$ measured by the TEOM monitor (Fig. R6a, 1-24 January, 2015), and the ratios of cations to anions in the four seasons of 2014 (Fig. R6b).

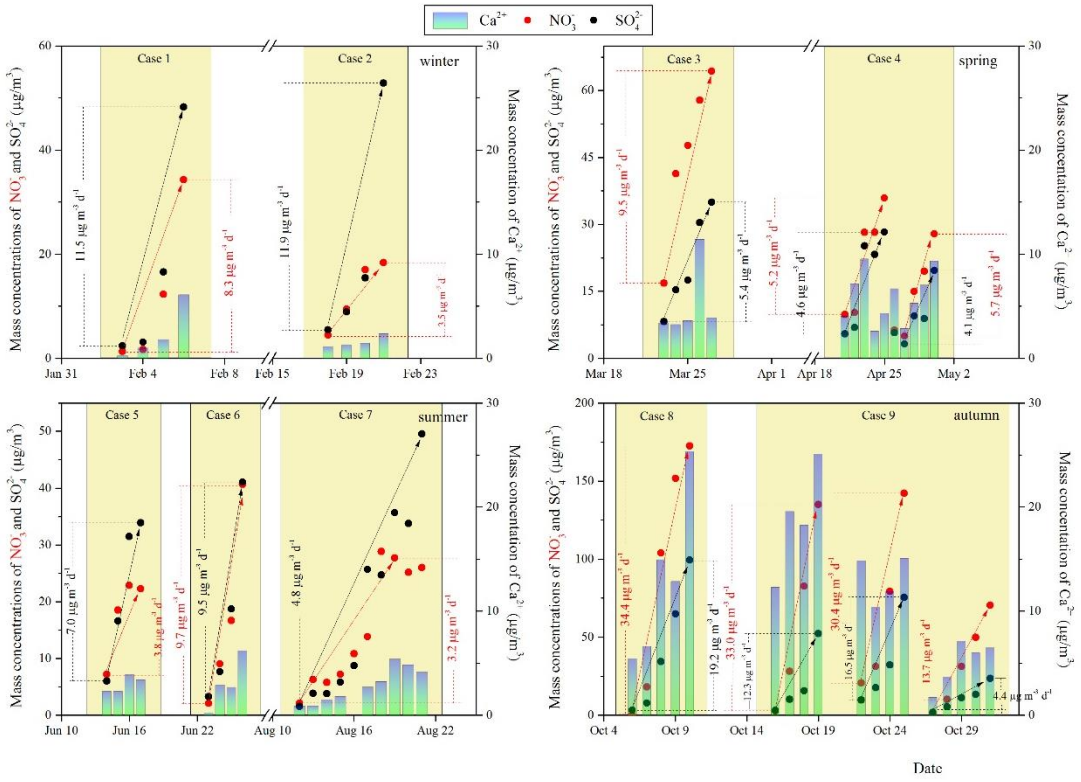


Fig. R7 Case studies about the increasing rates of NO_3^- and SO_4^{2-} with the elevation of Ca^{2+} during serious pollution events in the four seasons.

A list of all relevant changes made in the manuscript

Based on the valuable comments and suggestions of the three reviewers, the followings are a list of all relevant changes made in the manuscript.

1. The data of WSIs in $PM_{2.5}$ at the rural site during the year 2014 has been added in our revised manuscript.
2. Solid evidences about the impacts of farmers' activities (Cl^- from coal combustion by farmers, fertilization of NH_4Cl as well as Ca^{2+} from maize harvest and soil ploughing and so on) on regional air quality have been added in our revised manuscript.
3. The molar composition of WSI under different pollution levels and the comparison between WSIs and $PM_{2.5}$ have been delated in our revised manuscript due to being away from the topic of the manuscript.
4. The specification about the data quality assurance has been added in our revised manuscript.
5. Most of figures have been amended for supporting the results and discussion in the manuscript.
6. Some logical and grammatical mistakes have been corrected in our revised manuscript.
7. Several references have been inserted to confirm our points in our revised manuscript.

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 d~~Daily samples of $PM_{2.5}$ were collected in Beijing city as well as a rural area in Baoding, Hebei Province through the year of 2014, and the seasonal variation characteristics of water-soluble ions (WSIs) in the $PM_{2.5}$ were comprehensively analyzed for recognizing their possible sources. The results indicated that the periodic emissions from farmers' activities made evident contribution to the atmospheric WSIs in Beijing. The relatively high concentration of K^+ in winter and autumn ~~further~~at the two sampling sites confirmed that crop straw burning made evident contribution to atmospheric K^+ ~~$PM_{2.5}$~~ 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~~in~~ winter in Beijing were reasonably~~was~~ ascribed to coal combustion for heating by farmers. The unusually high ratio of Cl^- to Na^+ in summer, the obviously high concentrations of Cl^- in the rural sampling site and the elevation of Cl^- proportion in WSIs in Beijing during the maize fertilization could be rationally explained by the use of the prevailing fertilizer~~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 abnormally high concentrations of Ca^{2+} at the two sampling sites and the elevation of Ca^{2+} proportion during the period of the maize harvest and soil ploughing in Beijing provided convincing evidences that the intensive agricultural activities in autumn made evident contribution to the regional mineral dust. The most serious pollution episodes in autumn were coincident with significant elevation of Ca^{2+}, indicating that~~which was ascribed to be from harvest of the summer maize and tillage for planting the winter wheat. The~~ the mineral dust emission from the harvest and soil ploughing~~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., 2014a;Yang et al., 2015b;Zhang et al., 2015b;Zheng et al., 2015b;Sun et al., 2006). The severe haze pollution is mainly ascribed to elevation of fine particulate matter with dynamic diameter less than 2.5μm ($PM_{2.5}$)~~, usually called $PM_{2.5}$~~ (Huang et al., 2014a). $PM_{2.5}$ can directly reduce atmospheric visibility by scattering or absorbing solar light (Seinfeld and Pandis, 1998;Buseck and Posfai, 1999;Cheng et al., 2006) and is harmful to human health (Finlayson-Pitts and Pitts, 2000;Nel, 2005;Poschl, 2005;Peplow, 2014). To mitigate the serious pollution status, identification of the sources of $PM_{2.5}$ is urgently needed for the effective control measures. Based on field measurements, positive matrix factorization (PMF) (Yu et al., 2013;Wu et al., 2014;Huang et al., 2014a), principal component analysis (PCA) (Wang et al., 2015) and chemical mass balance (CMB) (Huang et al., 2014a;Guo et al., 2012) have been widely used for identifying the sources of $PM_{2.5}$. However, the results of the source apportionment are still not convincing because there are large uncertainties about the indicators, dominant factors and emission inventories used for the identification. For example, some studies suggested traffic emissions in Beijing contributed about 15~20% to the $PM_{2.5}$ (Yu et al., 2013;Wu et al., 2014), while only 4% of the contribution was also reported (Zhang et al., 2013)~~(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 residential~~domestic~~ coal stoves on both the emission intensity~~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 mainly focus on June-July and October-November and residential~~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 mostly~~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 (Bealey et al., 2007; Ji et al., 2013), the abrupt release of the particles by smashing crop straw for returning in the vast area of the

NCP must also make striking contribution to atmospheric particles in the region during the seasonal harvest seasons. In winter, the serious pollutant emissions from the chimney of the farmers' coal stoves can be easily imagined by the strong smog. Although residential~~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 intensity~~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 by farmers mainly concentrates on the four months in winter.

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

2. Materials and methods

2.1. Sampling sites

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

694 from industries, traffic and commercial emissions. The distance between the two sampling sites is
695 about 170km and the detailed location of the two sampling sites is presented in Fig. 1.

696 **2.2. Sample collection**

697 $PM_{2.5}$ samples at the two sites were both collected on Millipore PTFE filters (90mm) by an artificial
698 intelligence's $PM_{2.5}$ sampler (LaoYing-2034) and the sampling flow rate was set to 100L min^{-1}. The
699 duration of each sampling was 24 hours, started at 3:00 p.m. every day and ended at 3:00 p.m. on
700 the next day. All the samples were put in dedicated filter storage containers (90mm, Millipore) after
701 sampling and preserved in a refrigerator till analysis. For the sampling site of RCEES, A total of
702 235 $PM_{2.5}$ samples were collected from January to November of 2014, in winter (Jan 9- Mar 15
703 ~~2014~~), spring (Mar 16- May 31~~ 2014~~), summer (Jun 1- Jun 30, Aug 9- Aug 21~~ 2014~~) and autumn
704 (Sep 19- Nov 14~~ 2014~~). To explore the possible influence of farmers' activities, $PM_{2.5}$ samples at
705 DBT were mainly collected during the periods of periodic farmers' activities: heating season in
706 winter (Jan 9- Feb 25), harvest seasons in summer (Jun 9- Jun 22, Aug 9- Aug 17) and autumn (Sep
707 19- Oct 18, Oct 28- Nov 14).

708 **~~2.2~~ 2.3. ~~Ion~~ Sample analysis**

709 ~~Sample~~ Each sample ~~and blank~~ filters were extracted ultrasonically with 10mL ultrapure water for
710 half an hour. The solutions were filtered through water micro-porous membrane (pore size, 0.45μm;
711 diameter, 13mm) before analysis and the water-soluble ions (WSIs) in the treated filtrates were
712 analyzed by Ion Chromatography (IC, WAYEE IC6200). Five anions (F^-, $HCOO^-$, Cl^-, NO_3^- and
713 SO_4^{2-}) were separated by using an anion column (IC SI-52 4E, 4mmID*250mm) with the eluent
714 (3.6mmol L^{-1} Na_2CO_3) flow rate of 0.8mL min^{-1} and column temperature of 45 ℃. Five cations
715 (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. At least three filter blanks were analyzed for 60 filter samples, and the average blank values were about 0.03mg L^{-1} for Na^+, Ca^{2+}, F^-, NO_3^- and SO_4^{2-}, 0.02mg L^{-1} for NH_4^+ and Cl^-, 0.01mg L^{-1} for Mg^{2+}, K^+ and $HCOO^-$. The concentrations of all the ions were corrected for blanks.~~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~~2.4. Meteorology, trace gases and back trajectory

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

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

~~**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~~

~~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

The ratios of total cation concentration to total anion concentration in different seasons are illustrated in Fig. 2a. The near unity of the ratios indicated excellent charge balance in $PM_{2.5}$ and high quality of the data. The mass concentrations of WSIs and $PM_{2.5}$ at the sampling site of RCEES during the period of Jan 1- Jan 24, 2015 were also simultaneously measured by the filter sampling method and the TEOM 1405 Monitor, respectively. ~~for 24 days (Jan 1- Jan 24, 2015).~~ As shown in ~~Fig. 1a and Fig. 1b~~Fig. 2b, the variation trends of the WSIs and $PM_{2.5}$ were almost the same with a correlation coefficient (R^2) of ~~0.908~~0.91, 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, which was much greater than the values of 50-60% reported by previous studies~~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). Therefore, ~~The~~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). 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 its 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 total mass proportions of NO_3^- and NH_4^+ in WSIs usually accounts for about 50% in Beijing city (Yang et al., 2015a), whereas they were found to only account for about 20% in the filters of the TEOM 1405 Monitor, confirming the serious loss of NH_4NO_3 under the high temperature adopted by the TEOM 1405 Monitor.

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 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.~~

3.1. Daily variations of WSIs in Beijing city

~~3.2. Daily variations of WSIs in each season~~

The daily variations of WSIs at RCEES in each season are illustrated in ~~Fig. 2~~Fig. 3 and the statistic mass concentrations of the WSIs at RCEES are summarized in Table 1. It is evident that the daily variations of the WSIs at RCEES 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

804 the WSIs during the pollution episodes revealed strong sources of the pollutants around Beijing.

805 The mean concentrations (μg m^{-3}) of WSIs at RCEES in spring, summer, autumn and winter were

806 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

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

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

809 2015b). The three principal ions were mainly ascribed to secondary formation as discussed in the

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

811 and nitrate formation, the relatively low SO_2 concentration, the fast thermal decomposition of

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

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

814 summer. In comparison with other seasons, the remarkable elevation of atmospheric SO_2 and NO_x

815 (see section~~Sect.~~ 3.2.3) in winter would override the relatively low atmospheric photo-oxidants for

816 their oxidation rates and resulted in the highest mean concentration of WSIs. Although the

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

818 spring (see section~~Sect.~~ 3.2.3), the mean concentration of WSIs in autumn was almost the same as

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

820 dominated the secondary formation of the atmospheric principal ions (see section~~Sect.~~ 3.2.3).

821 **~~3.3.~~3.2. The possible sources for the WSIs**

822 ~~To disclose the contribution of possible sources to the WSIs, the molar composition of the WSIs,~~

823 ~~the seasonal variation characteristics of typical WSIs, the variation characteristics of the three~~

824 ~~principal ions during serious pollution episodes, the contribution of secondary formation to~~

825 ~~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 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.~~

To explore the possible contribution of the periodic emissions from farmers' activities to the WSIs in Beijing, the seasonal variation characteristics of typical WSIs at the urban and rural sites are comparatively illustrated in Fig. 4. It is evident that the seasonal variation of the typical WSIs at the two sites exhibited the similar trend, indicating the similar regional meteorological conditions. The concentrations of the typical WSIs at DBT were generally higher than those at RCEES during the periods of intensive farmers' activities (heating in winter, fertilization in summer and maize harvest in autumn). To reveal the air mass transport influence on the WSIs in Beijing, three-day backward trajectories for clusters and the corresponding mass concentrations of WSIs during the four seasons in Beijing were analyzed, and the results are illustrated in Fig. 5. It could be seen that the highest concentrations of the typical WSIs were usually observed in the air parcel from southwest/south regions with high density of population. Considering the large fraction (~30%) of air parcel from

the southwest/south regions in each season, the human activities in the southwest/south regions made evident contribution to the atmospheric WSIs in Beijing. Besides the industries, the emissions from the high density of farmers in the southwest/south regions of Beijing was also suspected to make evident contribution to the atmospheric WSIs in Beijing.

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

~~3.3.2. The seasonal variation characteristics of typical WSIs~~

~~It should be mentioned that~~Without considering the extremely high concentration of K^+ ~~in winter~~ on 1 February and 16 February (Fig. 4) ~~(Fig. 2) was~~ due to firework for celebrating Spring Festival and Lantern Festival ~~Chinese lunar year~~ (Jiang et al., 2015;Kong et al., 2015)~~.~~, ~~The seasonal variation characteristics of typical WSIs are illustrated in Fig. 4. For Cl^- and K^+, their high~~the concentrations of Cl^- and K^+ were much higher~~mainly occurred~~ in winter and autumn than in spring and summer at the two sites (Fig. 4). ~~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~~The molar ratio of Cl^- to Na^+ at the two sites measured by this study (~~Fig. 5~~Fig. 6) 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~~. 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~~in the two seasons~~ indicated that crop straw burning was a common source for K^+ and Cl^- (Li et al., 2014). However, only crop straw burning couldn't explain the relatively high concentrations of Cl^- in winter (Fig. 4), because the average mass Cl^-/K^+ ratio of 7.1 (except for firework event during the Spring Festival)

in winter was about a factor of 2 greater than the value of 3.8 in autumn when straw burning was prevailing in the region. Besides straw burning and sea-salt, coal combustion (Yu et al., 2013;Wu et al., 2014) and biofuel burning (Christian et al., 2010) have been also recognized as the sources for atmospheric Cl^-. Coal have almost been replaced with natural gas and electricity for heating during the winter before 2013 in Beijing city (http://www.radiotj.com/gnwyw/system/2014/07/22/000485853.shtml). Considering the relatively stable Cl^- emissions from coal combustion of industries and power plants as well as biofuel burning during the whole year, the obviously higher Cl^- concentrations measured in winter than in other seasons (Fig. 4) should be ascribed to the additional coal combustion by farmers because of the large amount of residential coal consumption (about 42,000,000 tons) in Beijing-Tianjin-Hebei region and ~~might be the circumstantial evidence for above suspicion.~~~~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 combustion ~~in China~~ (Huang et al., 2014b). ~~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, t~~The obviously higher Cl^- ~~concentrations measured~~proportion in winter than in ~~other seasons~~early spring (~~Fig. 2~~Fig. 7) provided further evidence for the above conclusion, because the proportion largely counteracted the influence of meteorological factors. ~~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.~~

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

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

3.2.2. The sources of Ca^{2+}

~~For Ca^{2+},~~ The remarkably high concentrations of Ca^{2+} – occurred in both spring and autumn at RCEES (Fig. 3 and Fig. 4), which were in good agreement with previous studies (Fig. 8). The evident elevation of Ca^{2+} concentrations in spring has been usually ascribed to the frequent dust storm (Zhao et al., 2013b), but there was still no explanation about the extremely high Ca^{2+} concentrations in autumn (Zhao et al., 2013b;Zhang et al., 2013). The intensive maize harvest and soil ploughing in autumn in the vast agricultural fields of the NCP were suspected to make contribution to atmospheric Ca^{2+} in Beijing. ~~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 atmospheric mineral particles were absorbed by crop leaves (Bealey et al., 2007; Ji et al., 2013) during crop growing season, especially in the North China where atmospheric mineral dust is always at high level (Zhang et al., 2013;Zhao et al., 2013b), a large fraction of the mineral dust absorbed on the leaves of crop ~~would~~ could be released into the atmosphere during harvest with crop straw being crushed into pieces for returning to fields which is a prevailing cultivation manner

under the advocacy of governments for reducing the influence of crop straw burning on the air quality. Additionally, the soil ploughing can also cause the suspension of particles (Fang et al., 2006; Chen et al., 2015). The remarkably high concentrations of Ca^{2+} during the autumn at DBT (Fig. 4) should be ascribed to the above agricultural activities because there are few construction activities in the rural area. Compared with the periods before and after maize harvest and soil ploughing, the proportion of Ca^{2+} during maize harvest and soil ploughing in autumn increased about 5%-7% (Fig. 7), confirming the influence of maize harvest and soil ploughing on atmospheric Ca^{2+} in Beijing. The back trajectory cluster analysis also supported the above conclusion: the extremely high concentrations of Ca^{2+} in Beijing occurred during the period of 6-25 October (Fig. 3 and Fig. 4) when the air parcels were mainly from the southwest/south regions (Fig. 5) where the vast areas of agricultural field were being under intensive maize harvest and soil ploughing; although the concentrations of Ca^{2+} in the rural area were still kept high levels during the period of 2-14 November (Fig.3 and Fig. 4), the relatively low concentrations of Ca^{2+} in Beijing were observed during the period when the air parcels were mainly from the northwest region (Fig. 5) where agricultural activities are relatively sparse.

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

~~For 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~~focus~~ on warmer seasons (Krupa, 2003), which cannot explain the frequently high concentrations of NH_4^+ observed in winter.~~.~~

~~However, the frequently high concentrations of NH_4^+ appeared in winter.~~ Besides the slow thermal decomposition of ammonium nitrate, strong NH_3 emission sources other than agricultural activities were suspected to be responsible for the frequently high concentrations of NH_4^+ in the cold winter. Besides ~~Emissions~~ NH_3 emissions ~~of NH_3~~ from vehicles ~~was regarded as an important source~~ (Liu et al., 2014)~~.~~. ~~In addition,~~ strong emission of NH_3 from ~~domestic~~ residential coal stoves (the NH_3 emission factor was 0.62-1.10g/kg coal) was indeed found by our preliminary measurements, which was in line with the latest study (Li et al., 2016). ~~(data were not shown)~~. During the serious pollution episodes, the concentrations of SO_2 at RCEES in autumn were almost the same as those in summer and about one magnitude lower than in winter (~~Fig. 6~~Fig. 9), but the peak concentrations of SO_4^{2-} in autumn were about ~~two times~~ a factor of 2 greater than those in summer and at almost the same level as those in winter. The gaseous phase reaction with OH (Zhao et al., 2013c;Quan et al., 2014), the heterogeneous reaction on mineral dust (He et al., 2014;Nie et al., 2014), and multiphase reactions in the water of particulate matters (Zheng et al., 2015a) of SO_2 have been recognized to be responsible for atmospheric SO_4^{2-} formation. The significant elevation of both Ca^{2+} and SO_4^{2-} in autumn implied that the heterogeneous reaction of SO_2 on the mineral dust might greatly accelerate the conversion of SO_2 to SO_4^{2-}. Although evidently high concentrations of Ca^{2+} occurred (Fig 3 ~~Fig. 2~~ and Fig. 4) in spring and SO_2 concentrations were much greater in spring than in autumn (~~Fig. 6~~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. 6~~Fig. 9). Similar to SO_4^{2-}, the relatively high concentrations of NO_3^- during the serious pollution events in autumn were also ascribed to the heterogeneous reaction of NO_2 on the mineral dust. Therefore,

the emission of mineral dust from maize harvest and soil ploughing in autumn also played important roles in secondary formation of nitrate and sulfate in Beijing.

The nitrogen oxidation ratio NOR = nNO_3^- / (nNO_3^- + nNO_x) (n refers to molar concentration) and the sulfur oxidation ratio SOR = nSO_4^{2-} / (nSO_4^{2-} + nSO_2) have been used to estimate the degree of secondary formation of NO_3^- and SO_4^{2-}, which can counteract the interference of meteorological factors (Chan and Yao, 2008;Yu et al., 2013;Guo et al., 2014;Huang et al., 2014a;Yang et al., 2015b;Zheng et al., 2015b). The values of NOR and SOR during haze days and non-haze days in four seasons are listed in Table 2. Both the values of NOR and SOR on non-haze days were found to be the highest in summer and the lowest in winter, well reflecting the seasonal variation of photochemical intensity. Although sunlight intensity greatly reduced at ground level during haze days, the values of NOR and SOR were about a factor of 2 greater during haze days than during non-haze days in the four seasons, implying again that the heterogeneous or multiphase reactions of SO_2 and NO_2 on atmospheric particles made significant contribution to atmospheric sulfate and nitrate.

~~3.3.3~~3.2.4. The variation characteristics of NO_3^- and SO_4^{2-} ~~the three principal ions~~ during serious pollution episodes

As shown in ~~Fig. 6~~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, ~~however~~ the detailed variation trends of SO_4^{2-} and NO_3^- were different, indicating that the elevation of SO_4^{2-} and NO_3^- was not simply ascribed to the physical process of accumulation. It is interesting to be noted that the increasing rates of SO_4^{2-} during some serious pollution events especially with elevation of Ca^{2+} (such as in spring and autumn)

were much slower than those of NO_3^- (Fig. 10), implying that the atmospheric heterogeneous reaction of NO_2 on the mineral dust ~~might be~~was faster than that of SO_2. ~~In comparison~~Compared with summer and winter, the relatively high ratios of NO_3^-/SO_4^{2-} in spring and autumn (~~Fig. 5~~Fig. 6) also supported the above ~~assumption~~conclusion.

~~3.3.4. Secondary formation for atmospheric sulfate and nitrate~~

~~The nitrogen oxidation ratio NOR = nNO_3^- / (nNO_3^- + nNO_x) (n refers to molar concentration) and the sulfur oxidation ratio SOR = nSO_4^{2-} / (nSO_4^{2-} + nSO_2) have been used to estimate the degree of secondary formation of NO_3^- and SO_4^{2-}, which can counteract the interference of meteorological factors (Chan and Yao, 2008;Yu et al., 2013;Guo et al., 2014;Huang et al., 2014;Yang et al., 2015b;Zheng et al., 2015b). The values of NOR and SOR during haze days and non-haze days in four seasons are listed in Table 2. Both the values of NOR and SOR on non-haze days were found to be the highest in summer and the lowest in winter, well reflecting the seasonal variation of photochemical intensity. Although sunlight intensity greatly reduced at ground level during haze days, the values of NOR and SOR were about a factor of 2 greater during haze days than during non-haze days in the four seasons, implying again that the heterogeneous or multiphase reactions of SO_2 and NO_2 on atmospheric particles made significant contribution to atmospheric sulfate and nitrate.~~

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

~~To reveal the air mass transport influence on the WSIs in Beijing, three-day backward trajectories for clusters and the corresponding mass concentrations of WSIs in each season were analyzed, and the results are illustrated in Fig. 7. It could be seen that the lowest concentrations of WSIs usually occurred in the northwest/northeast airflow with long distance transport. Because Beijing is~~

~~surrounded by mountains in the north/northwest/northeast directions where the population is sparse, these clusters brought the relatively clean air mass to accelerate the dissipation of aerosols. The highest concentrations of WSIs (especially for SO_4^{2-}, NO_3^- and NH_4^+) were usually observed in the air parcel from southwest/south regions with high density of population. Considering the large fraction (~30%) of air parcel from the southwest/south regions in each season, the human activities in the southwest/south regions made evident contribution to the atmospheric WSIs in Beijing. Besides the industries, the emissions from the high density of farmers in the southwest/south regions of Beijing was also suspected to make evident contribution to the atmospheric WSIs in Beijing, 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.~~3.3. Comparison with previous studies

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

Acknowledgements

This work was supported by the National Natural Science Foundation of China (21477142, 41203070 and 91544211), the "Strategic Priority Research Program" of the Chinese Academy of Sciences (XDB05010100) and the Special Fund for Environmental Research in the Public Interest (201509002).

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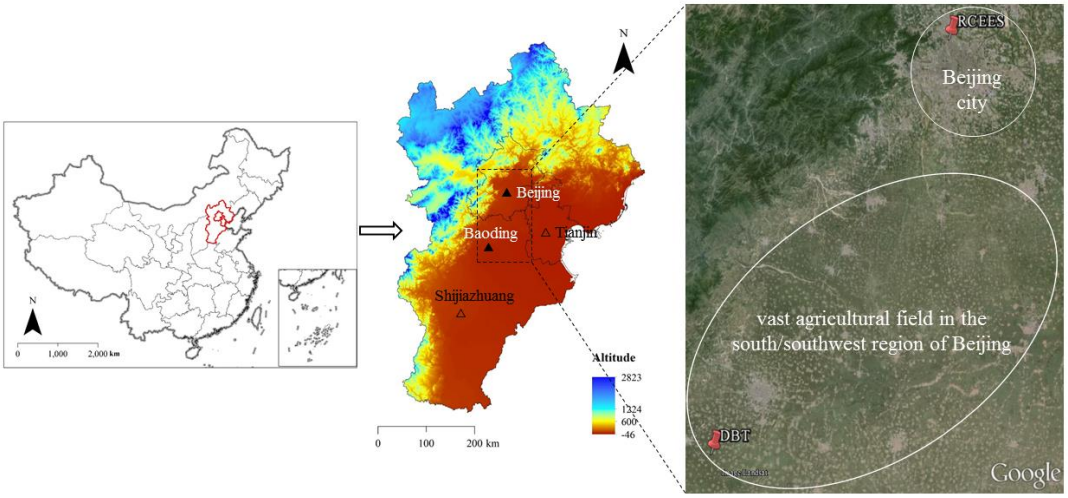


Fig. 1 Sampling sites (the urban site in Beijing city and the rural site in Baoding, Hebei Province) in the NCP.

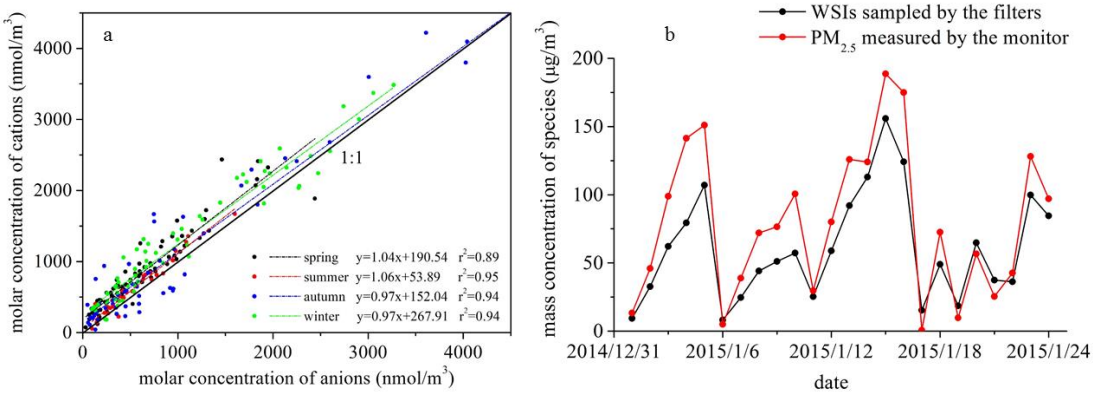


Fig. 2 The ratios of cations to anions in the four seasons of 2014 in Beijing (Fig. 2a), and the comparison between WSIs sampled by the filters and $PM_{2.5}$ measured by the TEOM monitor (Fig. 2b, 1-24 January, 2015).

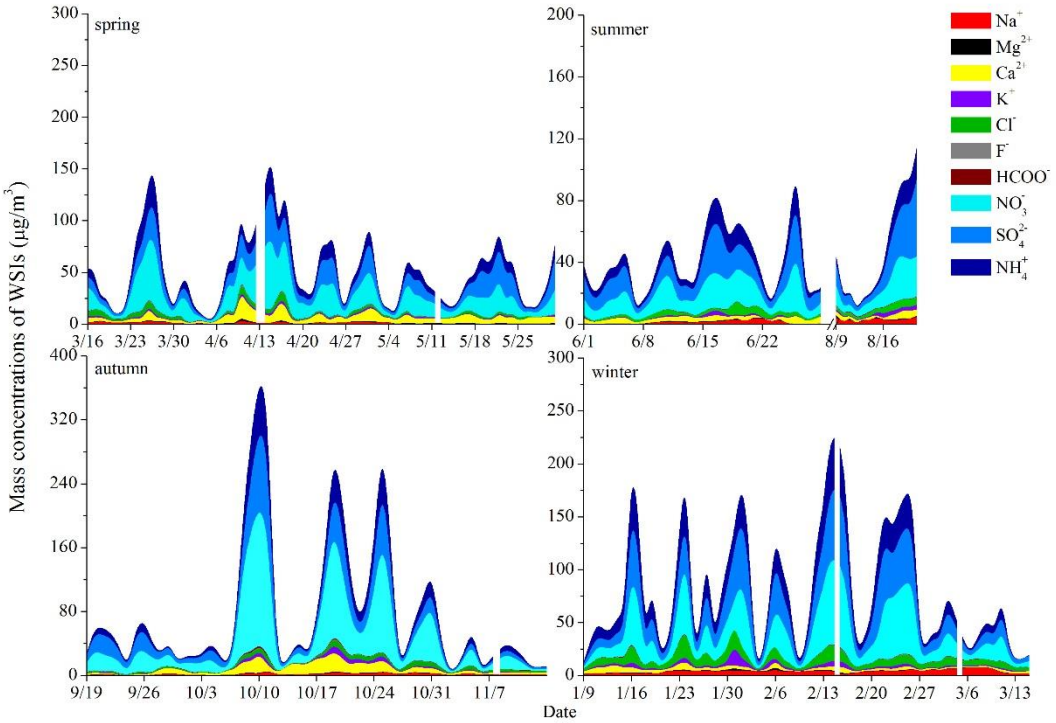


Fig. 3 Daily variations of WSIs in each season at RCEES (The smooth lines for the WSIs were drawn between the points of the daily data.).

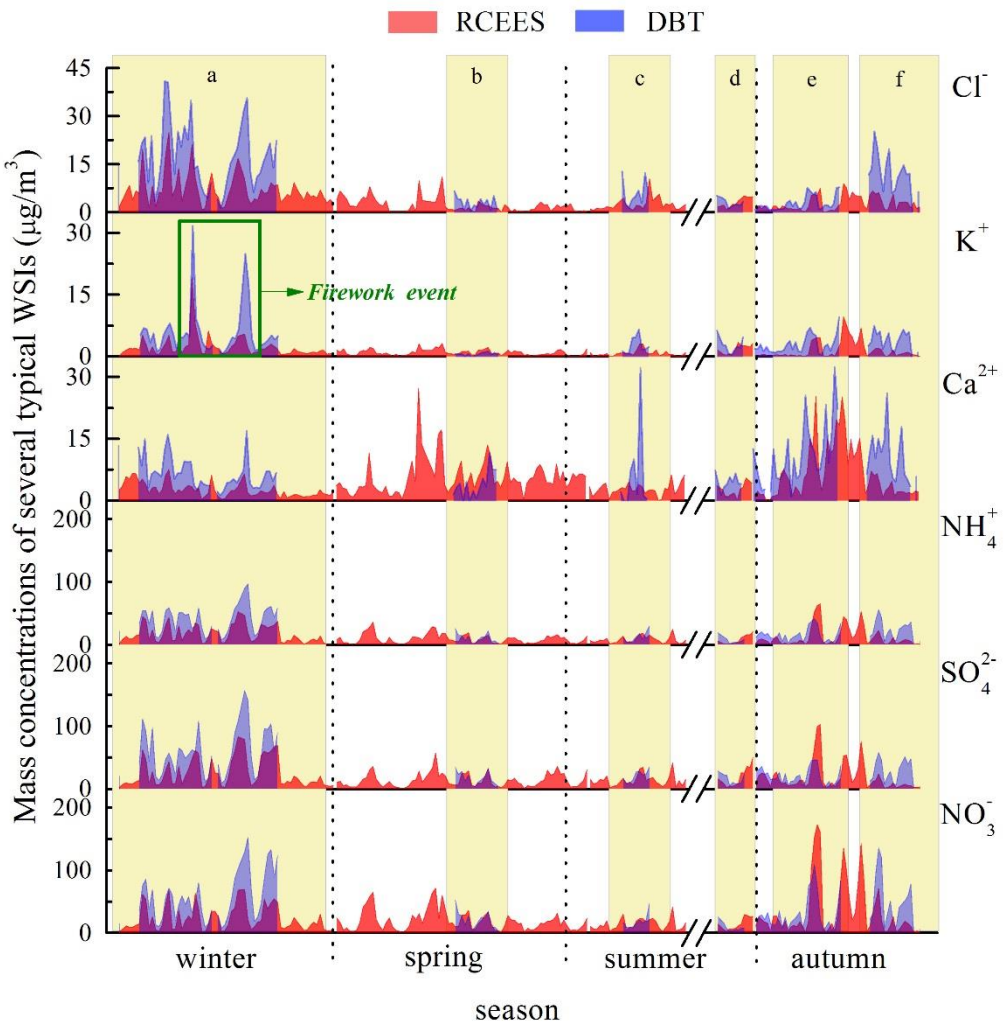


Fig. 4 Seasonal variations of the several typical WSIs in the year of 2014. (The mass concentrations of Cl^-, K^+, Ca^{2+}, NH_4^+, SO_4^{2-} and NO_3^- were presented at RCEES and DBT. The green square showed the firework event during the period of the Spring Festival. The gray square represented farmers' 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).)

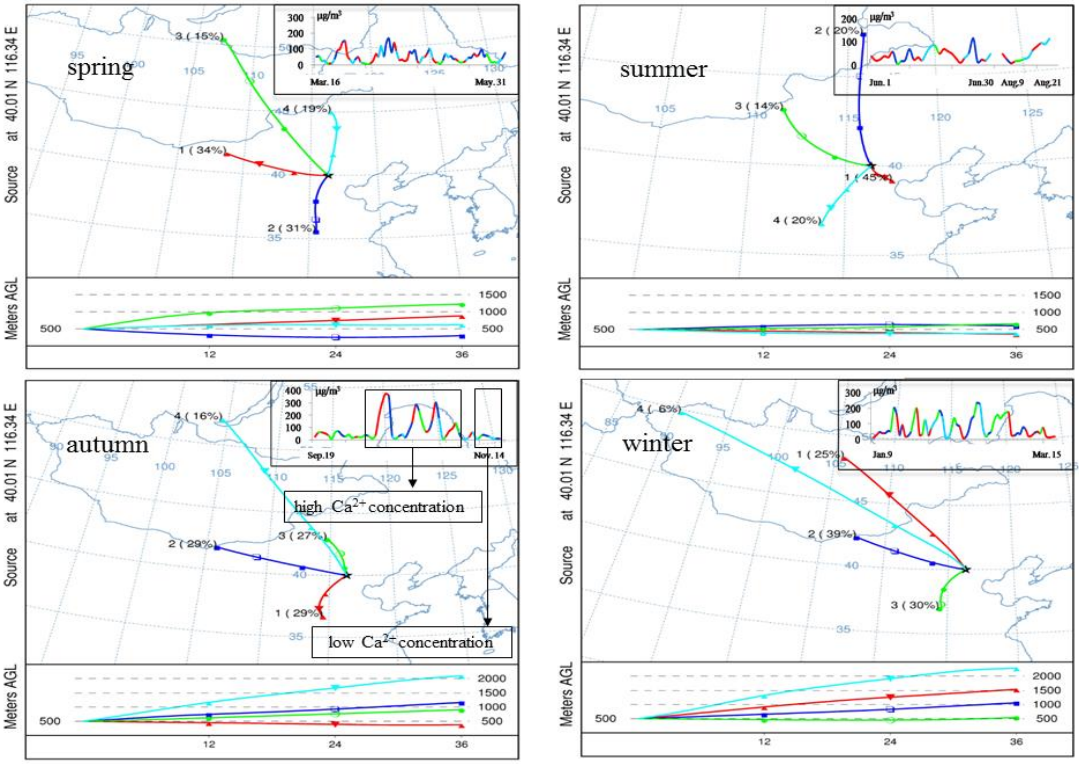


Fig. 5 The back trajectory cluster analysis and the corresponding overall ion mass concentration during the four seasons in Beijing.

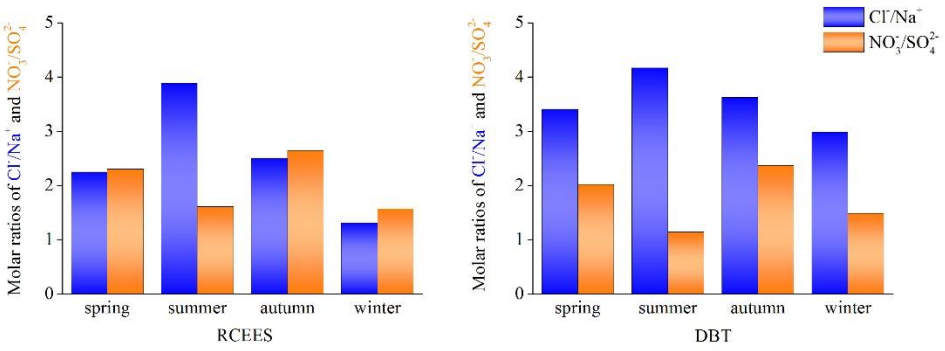


Fig. 6 The average molar ratios of Cl^-/Na^+ and NO_3^-/SO_4^{2-} in each season at the two sites.

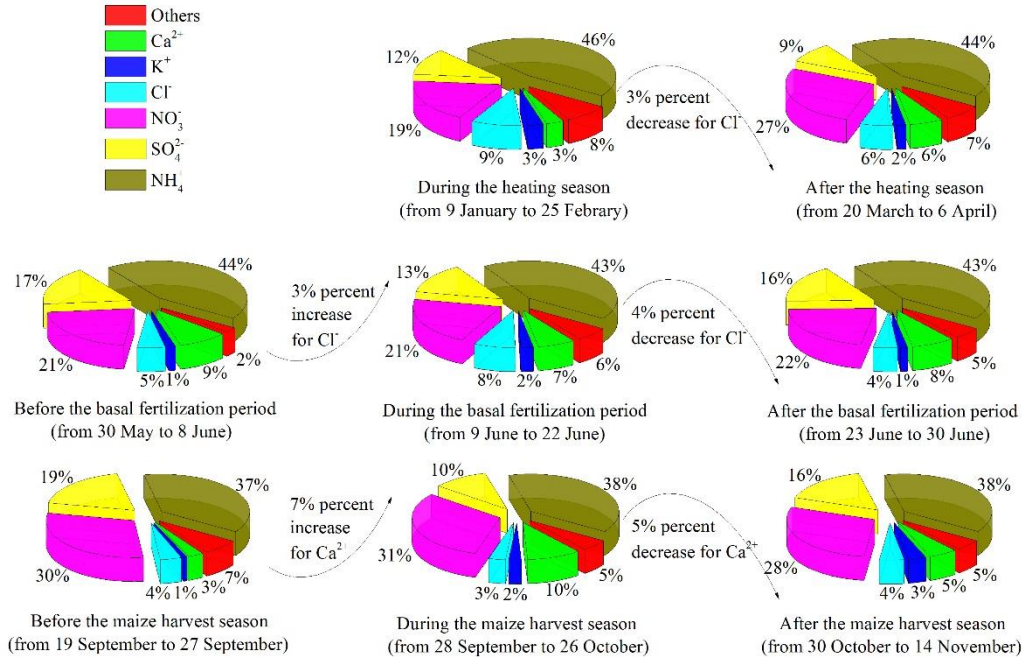


Fig. 7 Molar proportions of atmospheric WSIs at RCEES before, during and after the periods of heating in winter, maize fertilization in summer, and maize harvest and soil ploughing in autumn.

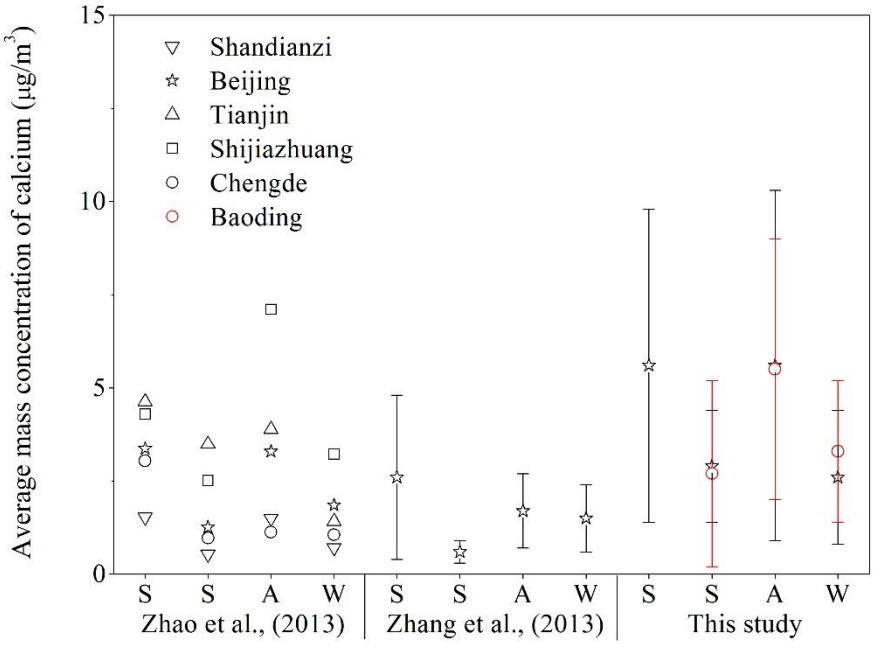


Fig. 8 Comparison of average mass concentration of calcium in four seasons between previous studies and this study for several cities in the NCP (S, S, A and W represent spring, summer, autumn and winter, respectively. The black symbols represent the urban sites and the red symbol represents the rural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

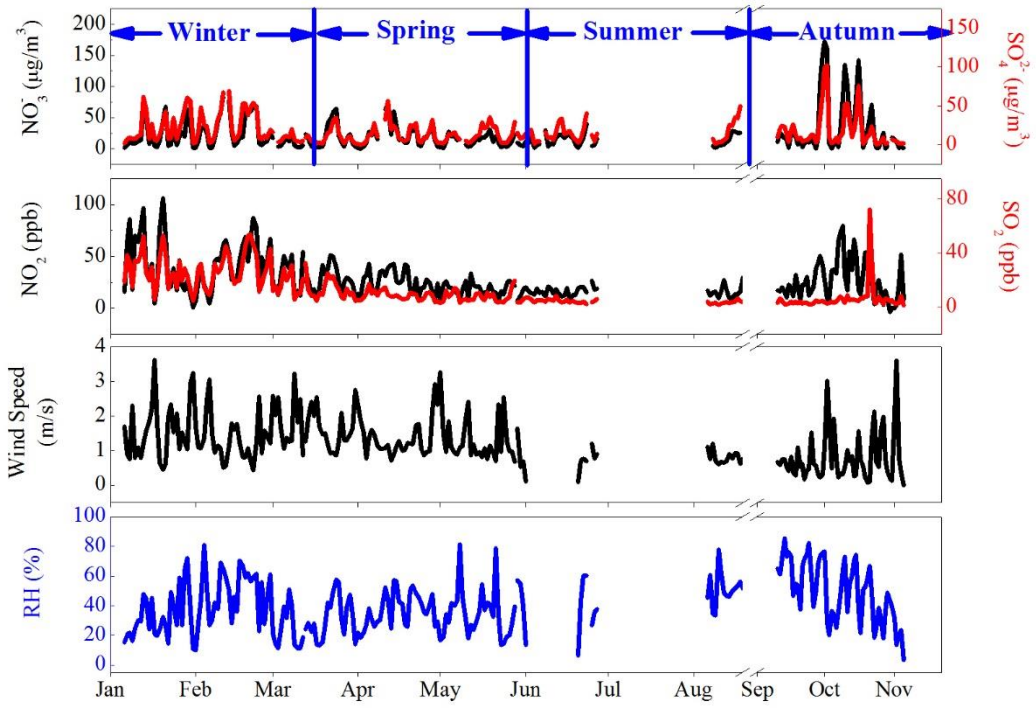


Fig. 9 Time series of NO_3^-, SO_4^{2-}, NO_2 and SO_2 and meteorological data (wind speed and relative humidity) during the four seasons in Beijing for 2014

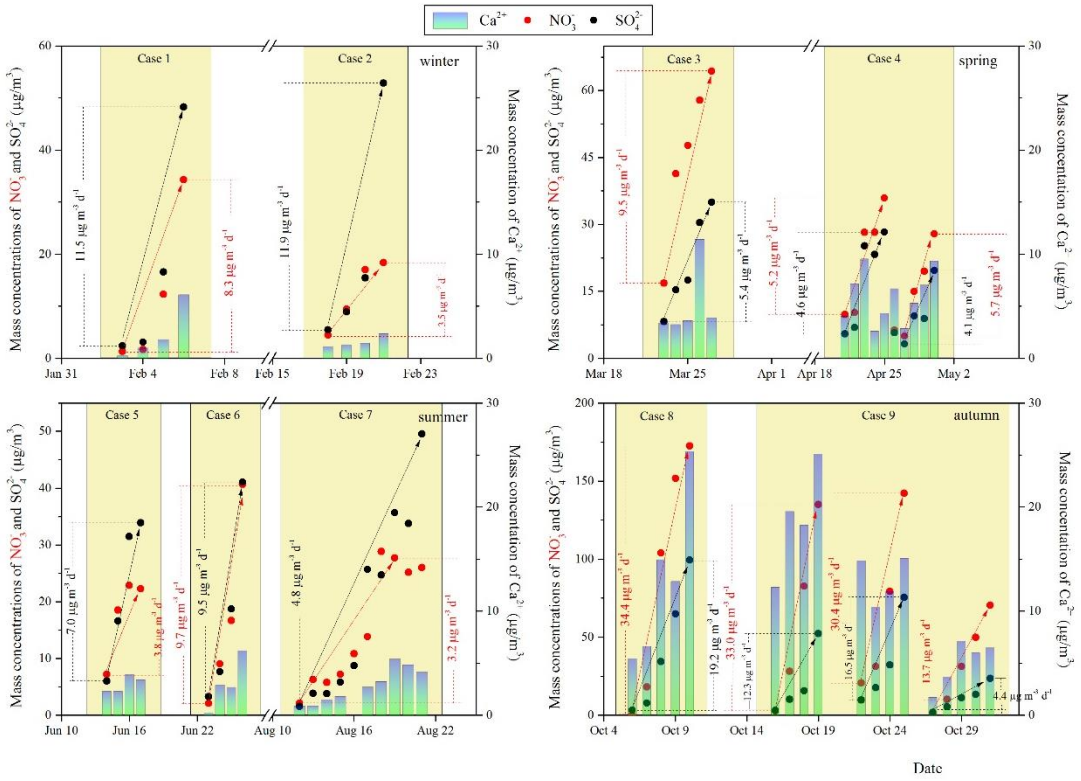


Fig. 10 Case studies about the increasing rates of NO_3^- and SO_4^{2-} with the elevation of Ca^{2+} during serious pollution events in the four seasons.

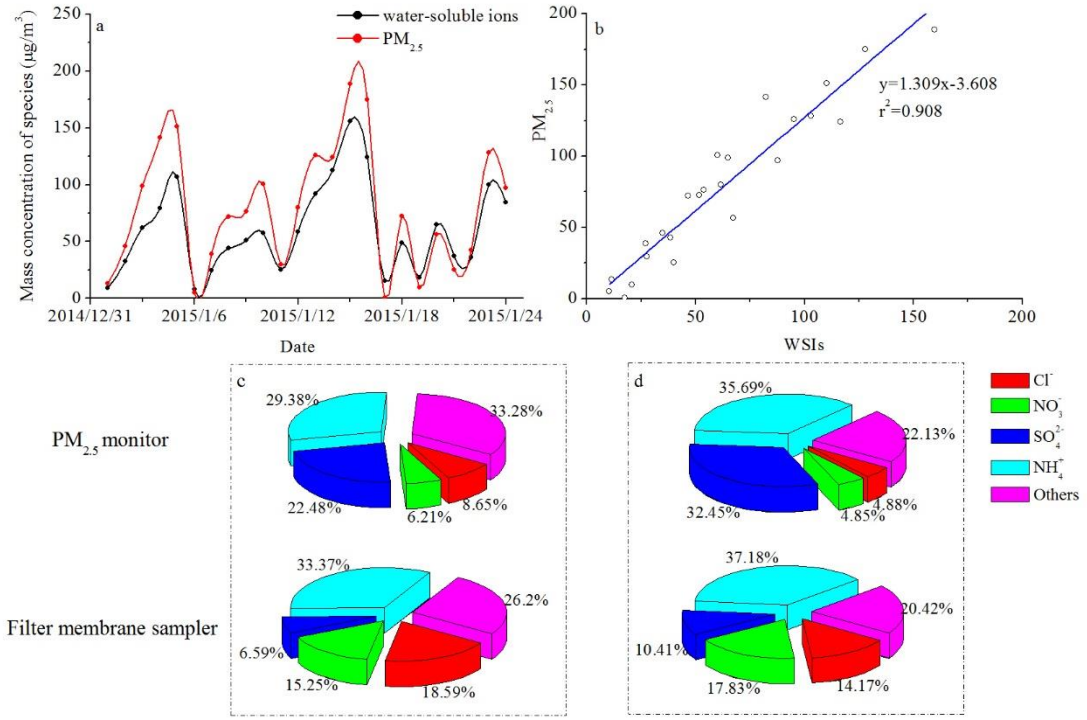


Fig. 1 Comparison between the filter sampling method and the $PM_{2.5}$ monitor for the daily average mass concentrations of the WSIs and $PM_{2.5}$ (Fig. 1a and 1b), and for the 12-day average molar composition of the WSIs on the filters collected by the two methods during the two 12-day sampling periods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

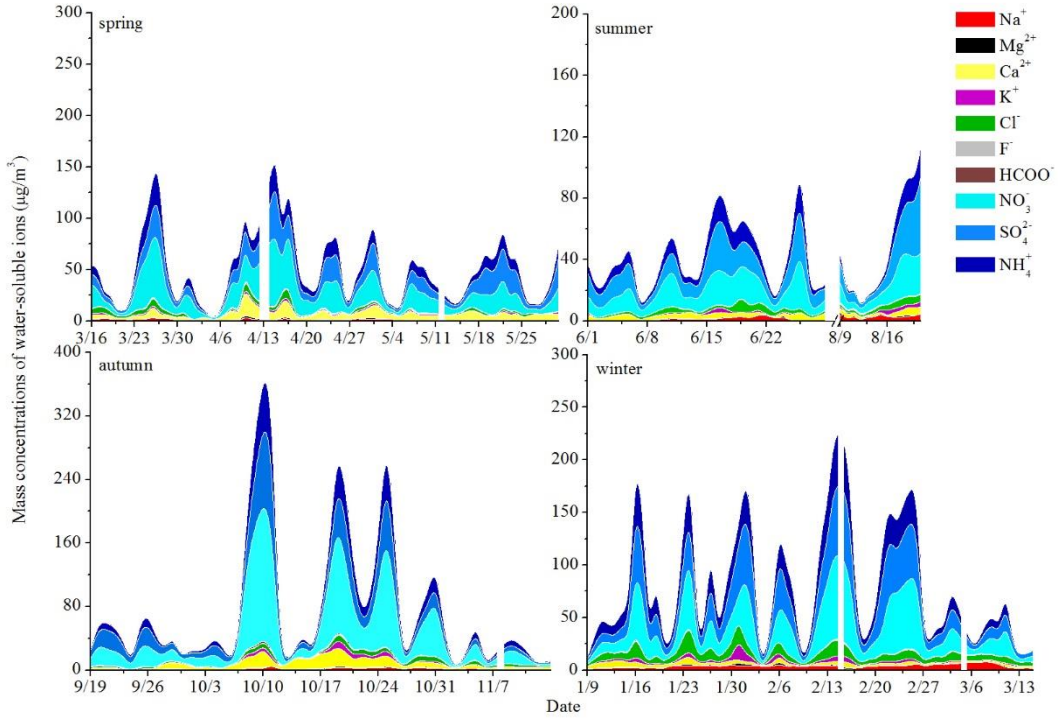


Fig. 2 Daily variations of WSIs in each season (the smooth lines for the WSIs were drawn between the points of the daily data).

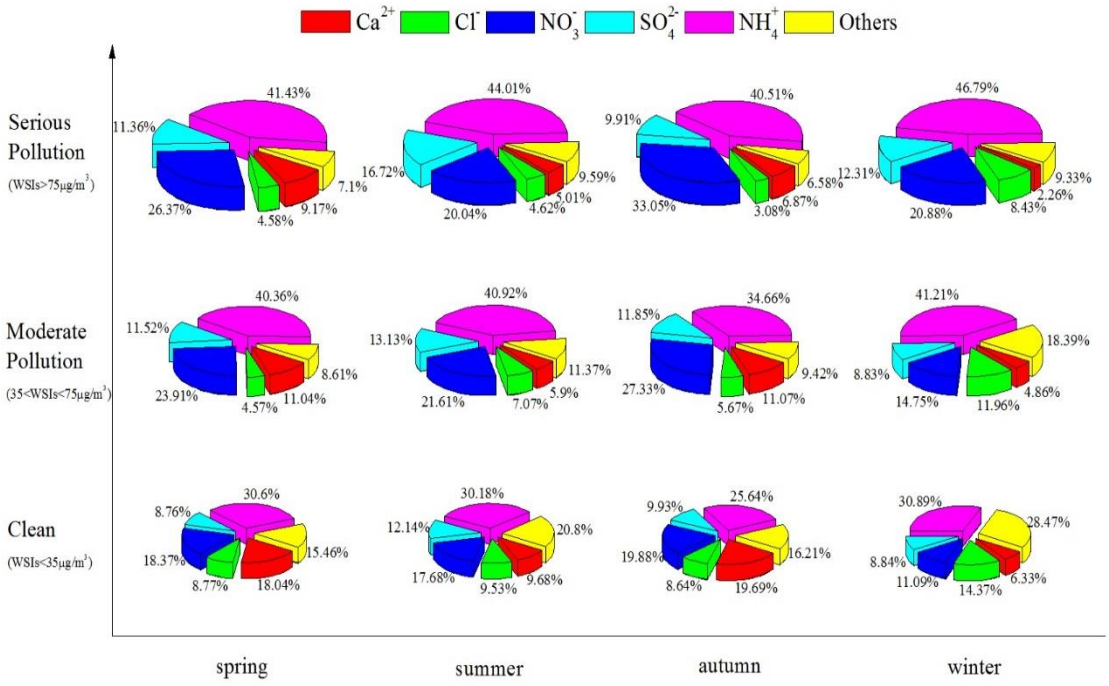


Fig. 3 Molar composition of the WSIs under different pollution levels in four seasons (Clean: WSIs < 35μg m^{-3}; Moderate pollution: 35μg m^{-3} < WSIs < 75μg m^{-3}; Serious pollution: WSIs > 75μg m^{-3})

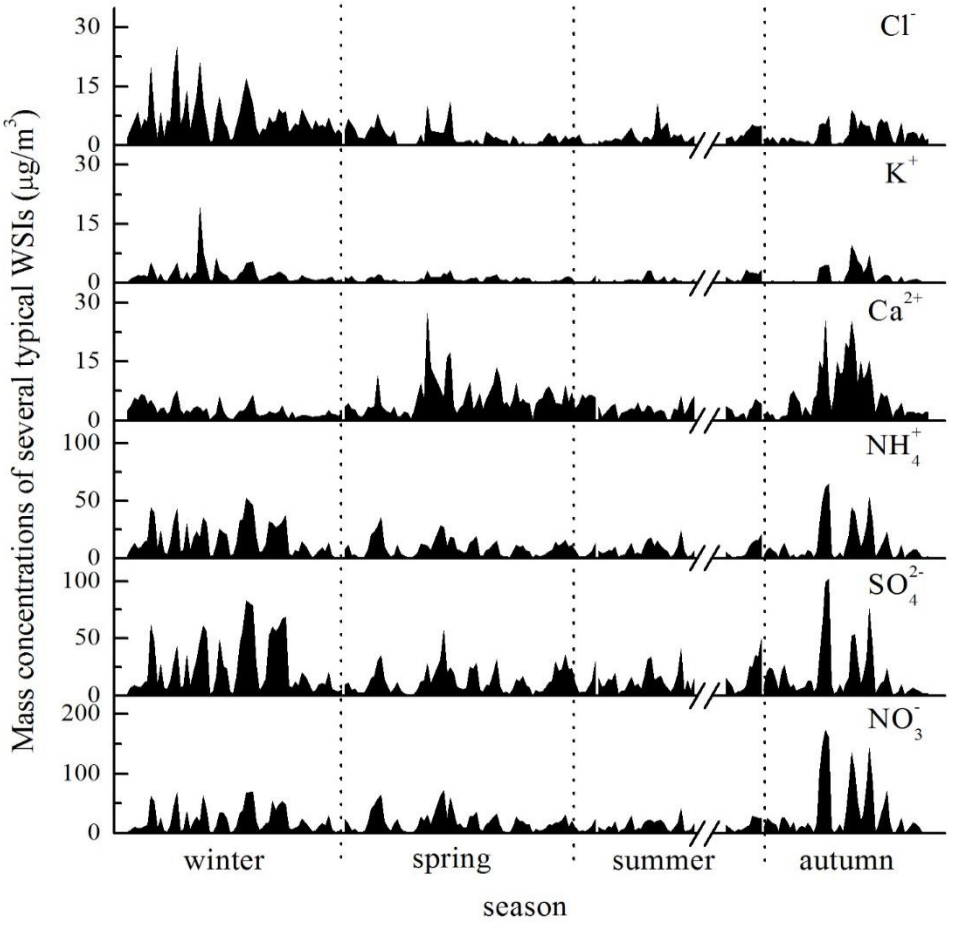


Fig. 4 The seasonal variations of the several typical WSIs in the year of 2014

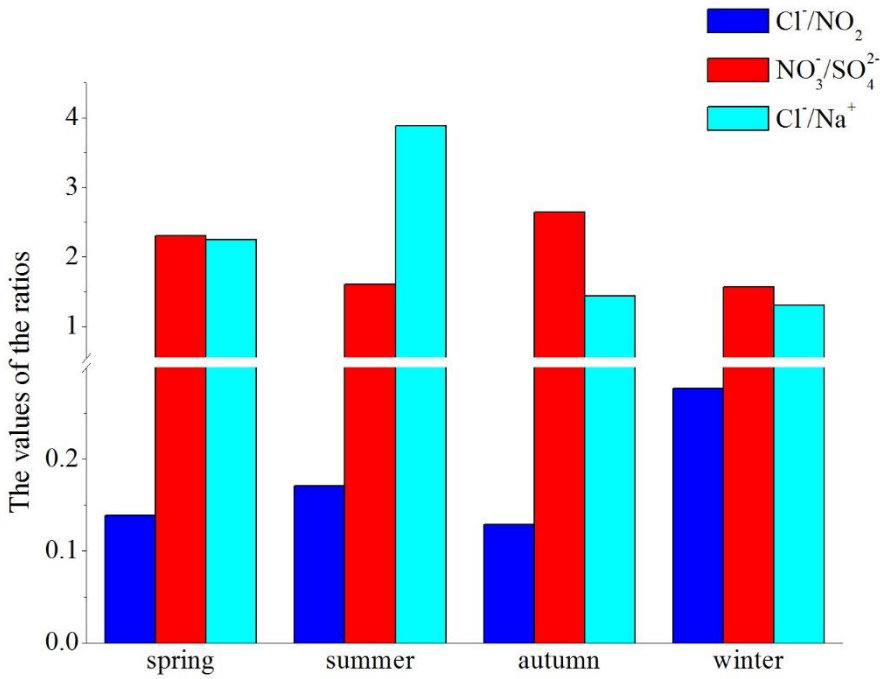


Fig. 5 the average ratio of Cl^-/NO_2 (the unit is $\mu g/m^3$ and ppb, respectively) and the average molar ratios of Cl^-/Na^+ and NO_3^-/SO_4^{2-} in each season.

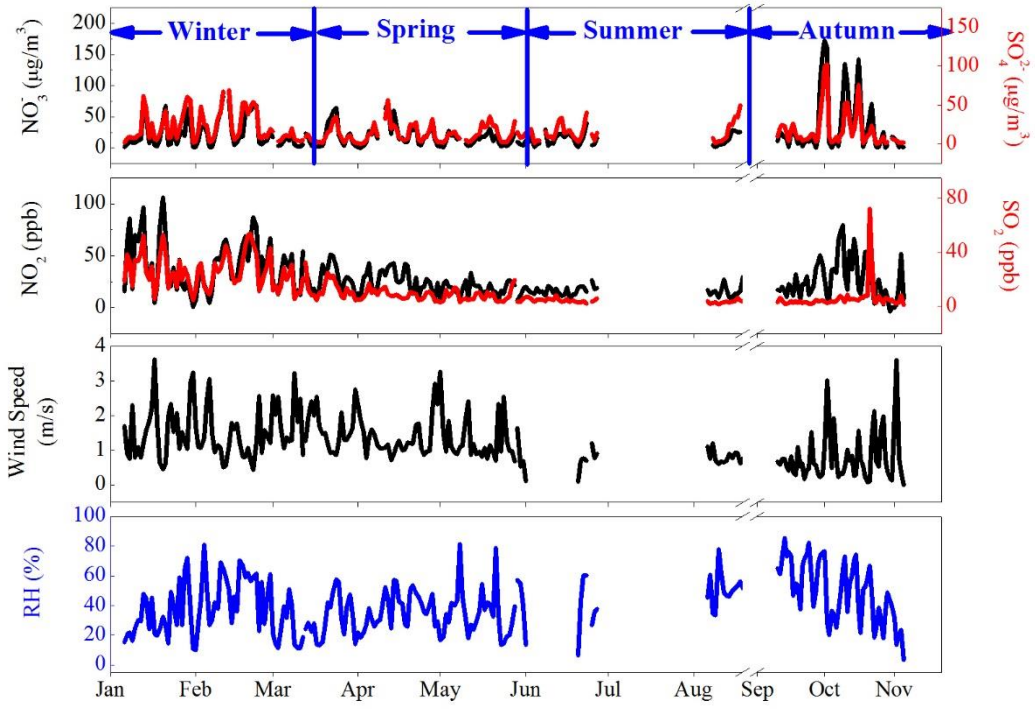
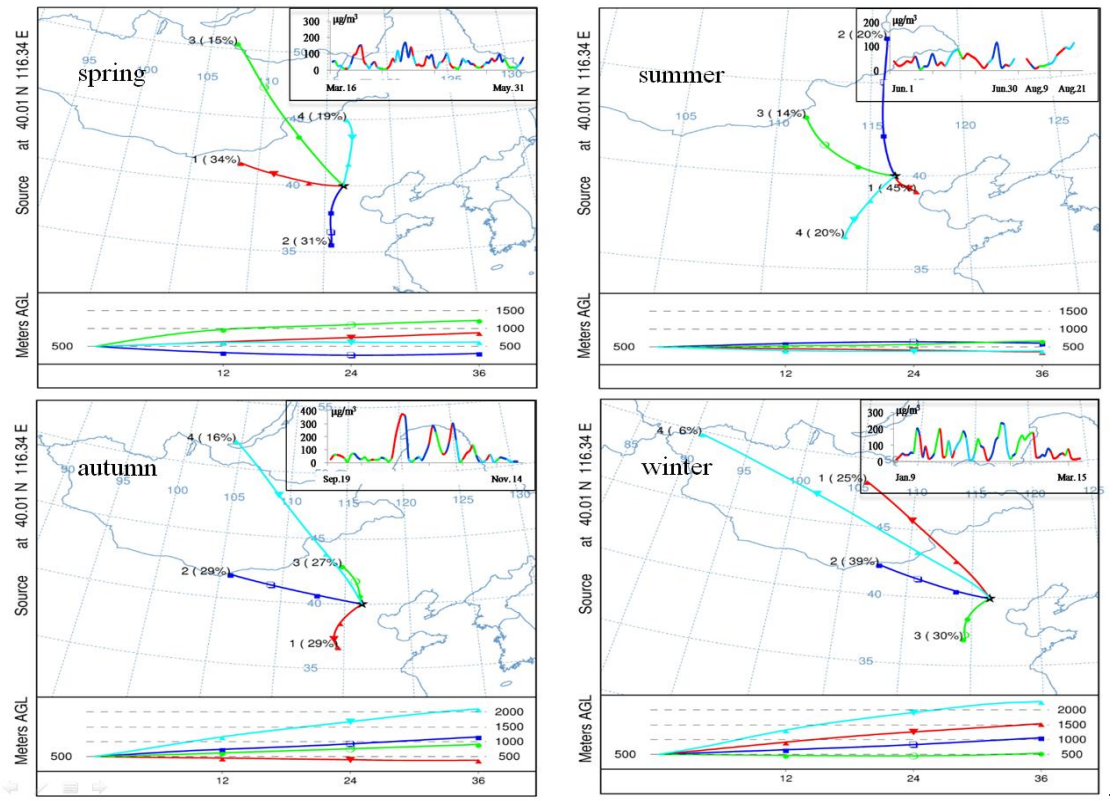


Fig. 6 Time series of NO_3^-, SO_4^{2-}, NO_2 and SO_2 and meteorological data (wind speed and relative humidity) in four seasons for 2014



~~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~~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

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.

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~~at RCEES.

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