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.

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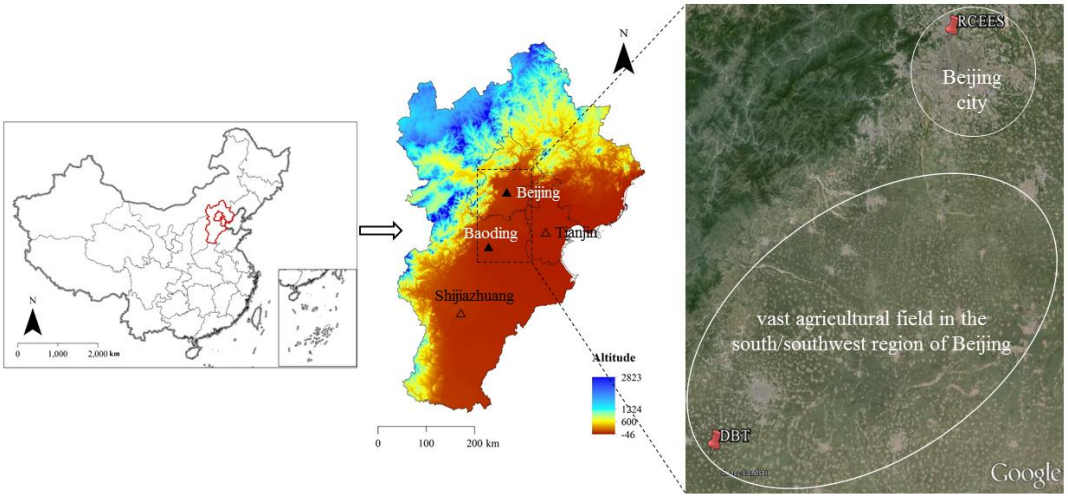

Fig. R1 Sampling sites (the urban site in Beijing city and the rural site in Baoding, Hebei Province) in the NCP.

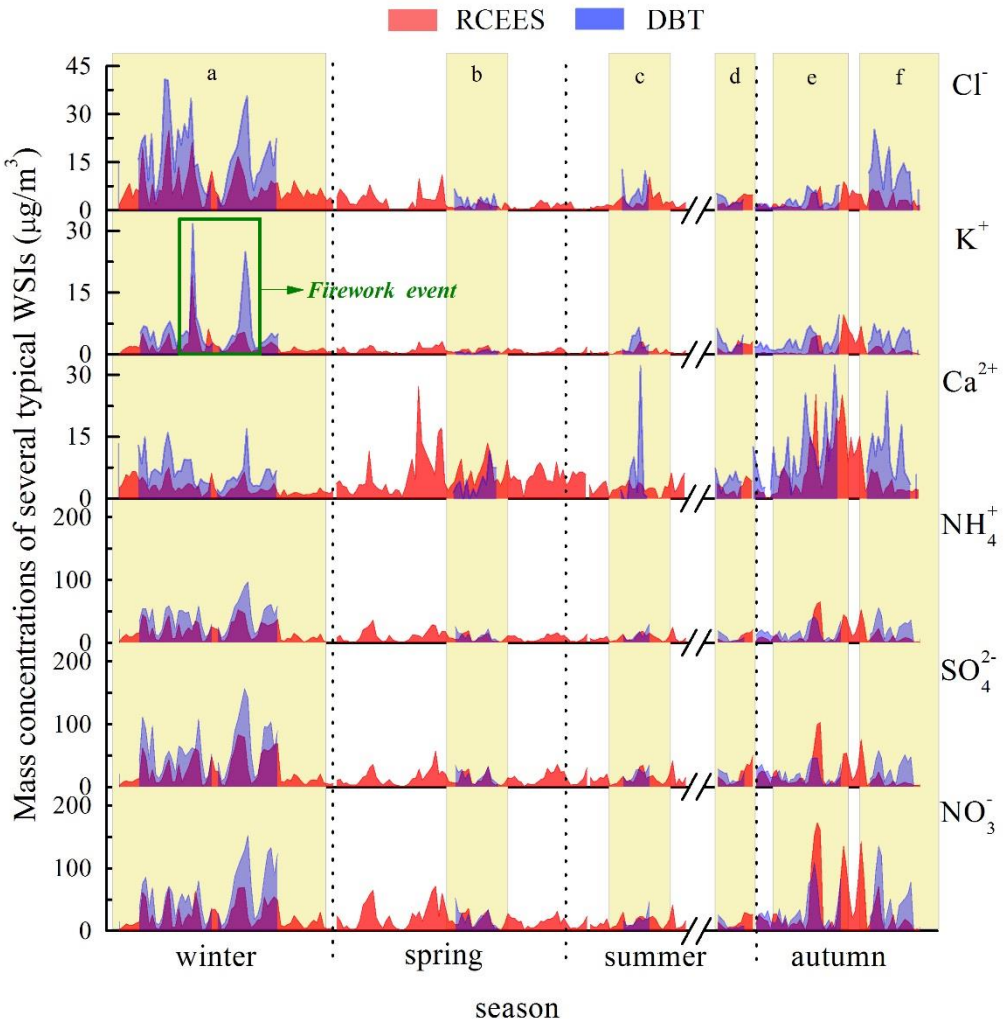

Fig. R2 Seasonal variations of the several typical WSIs in the year of 2014. (The mass concentrations of Cl^-, K^+, Ca^{2+}, NH_4^+, SO_4^{2-} and NO_3^- were presented at RCEES and DBT. The green square showed the firework event during the period of the Spring Festival. The gray square represented farmers'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

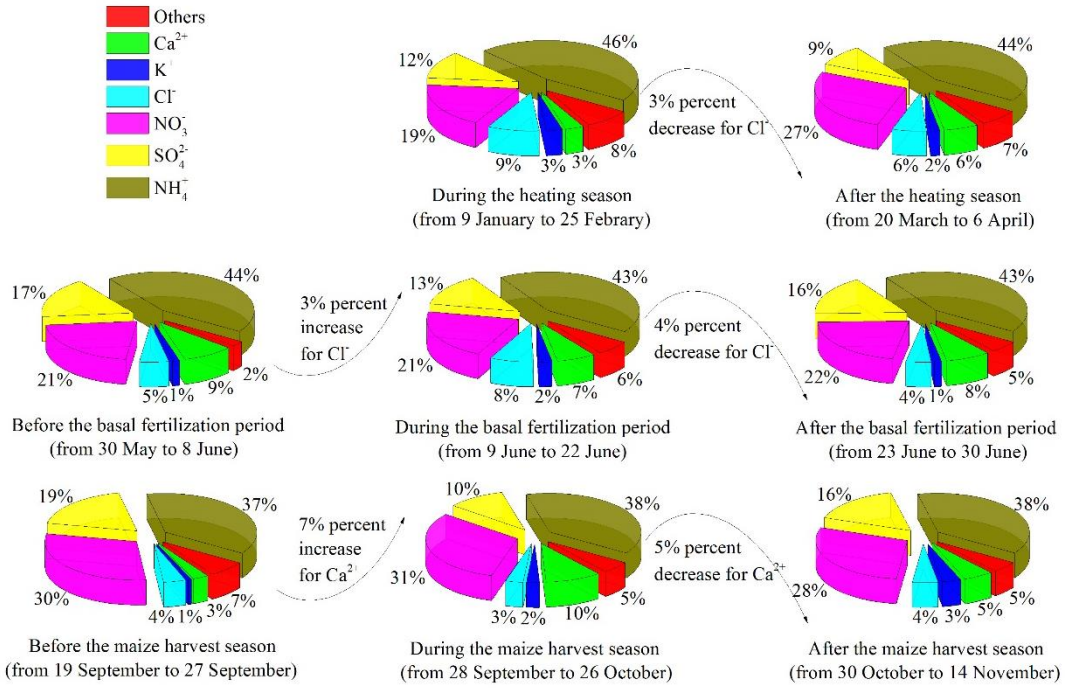

Fig. R3 Molar proportions of atmospheric WSIs in Beijing before, during and after the periods of heating in winter, maize fertilization in summer, and maize harvest and soil ploughing in autumn.

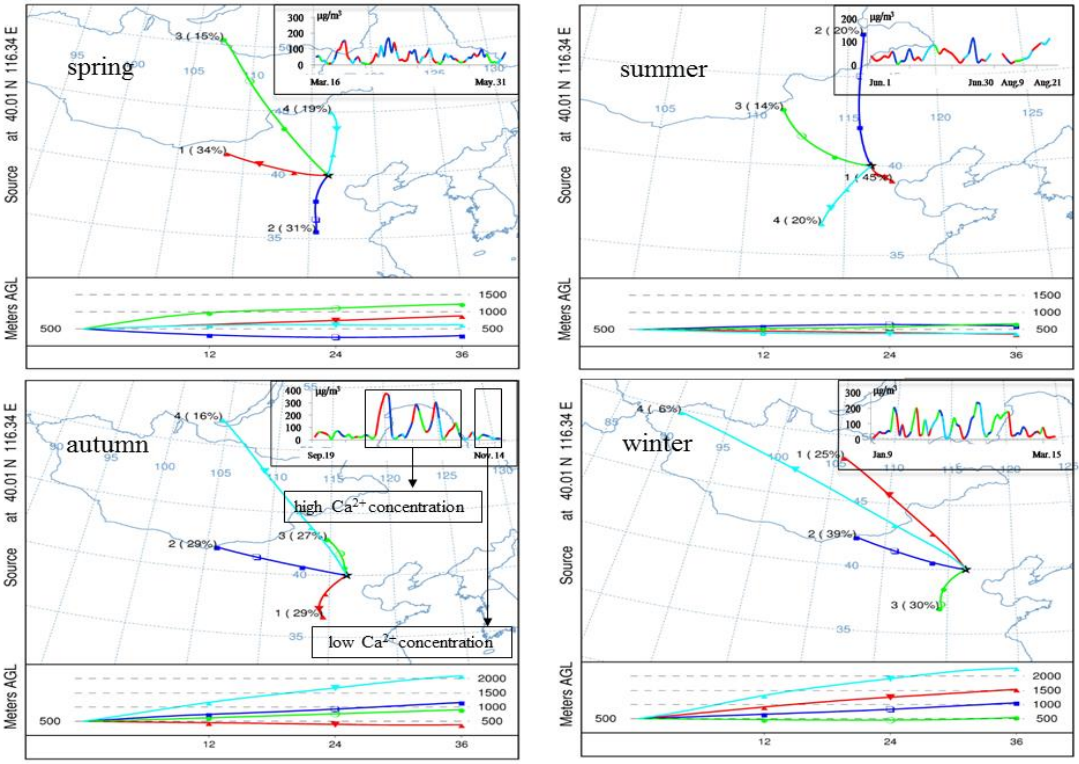

Fig. R4 The back trajectory cluster analysis and the corresponding overall ion mass concentration in four seasons.

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

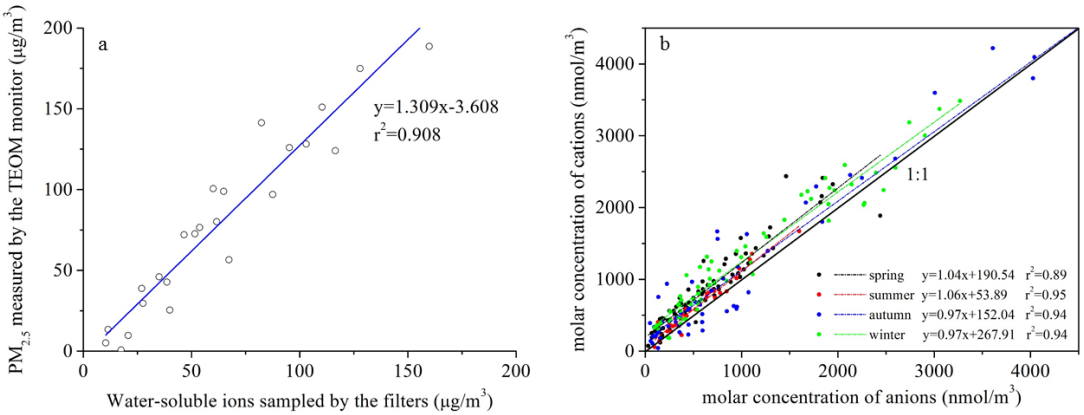

Fig. R6 The correlation between WSIs sampled by the filters and $PM_{2.5}$ measured by the TEOM monitor (Fig. R6a, 1-24 January, 2015), and the ratios of cations to anions in the four seasons of 2014 (Fig. R6b).

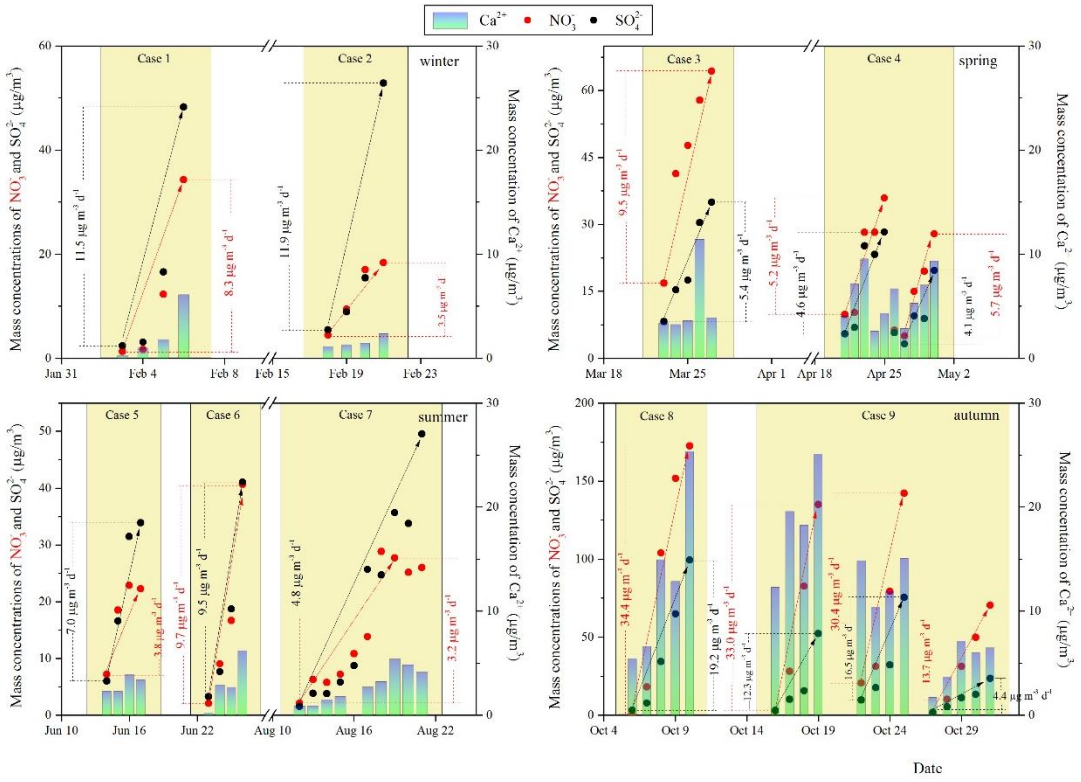

Fig. R7 Case studies about the increasing rates of NO_3^- and SO_4^{2-} with the elevation of Ca^{2+} during serious pollution events in the four seasons.