

## Response to Reviewer #1 by Yujing Mu et al.

Thank you for your comments. But we don't totally agree with your opinions. The followings are our responses to your comments.

**Comment 1:** So many studies have already been carried out for the chemical compositions from PM<sub>2.5</sub> 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. (the words marked in red are incorrect in English)

**Answer:** Although many studies have already been carried out for the chemical composition in PM<sub>2.5</sub> in Beijing, most of them focused on summer or winter, and only 5 of them conducted measurements in the four seasons. In addition, all of the studies only conducted measurements less than one month in one season. To reflect the seasonal variation characteristics of the water-soluble ions in detail, the daily measurements were conducted in this study except for July.

Although we didn't conduct other related aerosol measurements, the variation characteristics of the composition of the water-soluble ions in PM<sub>2.5</sub> were found to well reflect their possible sources, and the following important conclusions were derived from the measurements: 1. With the elevation of Ca<sup>2+</sup> in spring and autumn, the evidently faster increasing rates of NO<sub>3</sub><sup>-</sup> than SO<sub>4</sub><sup>2-</sup> implied that the atmospheric heterogeneous reaction of NO<sub>2</sub> on the mineral dust was an important source for NO<sub>3</sub><sup>-</sup>; 2. The obviously higher Cl<sup>-</sup> concentrations and the remarkably greater ratios of Cl<sup>-</sup> to NO<sub>x</sub> in winter than in other seasons indicated that coal combustion by farmers in winter made great contribution to atmospheric Cl<sup>-</sup> in Beijing; 3. The extremely high ratios of Cl<sup>-</sup> to Na<sup>+</sup> in summer implied that fertilization with ammonium chloride in the agricultural fields around Beijing might make evident contribution to atmospheric Cl<sup>-</sup>; 4. The coincidence of the remarkable elevation of Ca<sup>2+</sup> with the intensive harvest of maize and tillage of the agricultural fields in the vast rural areas around Beijing revealed that the harvest and tillage made striking contribution to atmospheric Ca<sup>2+</sup> in Beijing. Because the typical ratios of atmospheric pollutants have been widely used for identifying the sources of the pollutants, the above conclusions based on the remarkable variation characteristics of typical ratios were not simply from speculation. 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<sub>2</sub> 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.

**Comment 2:** On the whole, this paper is not suitable for publication in the ACP.

**Answer:** Because field measurement is one of the main subject areas of the ACP and there are original findings (comment 1) in the paper, we wondered why you say that the paper is not suitable for publication in the ACP.

**Comment 3:** 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:** “Farmer” is a commonly used word to represent people who are living in rural areas (Pattey et al., *Journal of the Air & Waste Management Association*, 2012:62(7); Mahmud, *Geofizika*, 2009:26(1)), why did you say “the use of the word “farmer” is inaccurate, even ridiculous”? We don’t think it is polite to use the word “ridiculous” in your comment. We don’t understand your meaning about the description of “agricultural activities” in the two sentences. Because the “rural area” was used for representing the countryside in the text of the paper, why did you request us using the “rural area” to describe the exact meaning? 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 meaning.

**Comment 4:** 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<sub>2.5</sub>. And the smashing process of crop straw could not be an important source of PM<sub>2.5</sub>. Just a small amount coarse PM might be emitted.

**Answer:** We don’t think the reviewer know that plants play an important role in PMs (including PM<sub>10</sub> and PM<sub>2.5</sub>) uptake (Bealey et al., *Journal of Environmental Management*, 2007:85(1); Ji et al., *Science China*, 2013:43(8)). There are about 300,000 km<sup>2</sup> agricultural fields where the harvest of winter wheat or summer maize only lasts about two weeks in the North China Plain, and hence one can imagine the huge emission of mineral dust during the harvest in the photo of the attachment. The evident elevation of Ca<sup>2+</sup> in PM<sub>2.5</sub> was also found during the summer maize harvest season in the rural area and Beijing city in 2014 (the figure in the attachment).

**Comment 5:** 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:** We don’t think “pollutants from coal combustion for heating” is more accurate for describing the meaning of the sentence, because “pollutants from coal combustion for heating” includes varies sources from industrial boilers, central-heating boilers as well as domestic coal stoves. In our opinions, it is better to replace “the farmers’ coal stoves” with “the domestic coal

stoves”. 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<sub>2</sub>O emissions for about ten years. Therefore, we are familiar with the rural areas very well.

**Comment 6:** 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<sub>2.5</sub> not to measure the mass concentrations of PM<sub>2.5</sub>, 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 7:** As mentioned in this paper, the TEOM 1405 is not suitable for accurate PM<sub>2.5</sub> 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<sub>2.5</sub> could not be obtained.

**Answer:** Because we lack the precision balance for weighing the filters, the mass concentrations of PM<sub>2.5</sub> were not measured. The mass concentrations of PM<sub>2.5</sub> can reveal the pollution levels, but not the detail information about their sources' origination. In this paper, the variation characteristics of the water-soluble ions provided the important information about the evident contribution of farmers' activities and heterogeneous reaction of NO<sub>2</sub> on mineral dust to the components of atmospheric PM<sub>2.5</sub> in Beijing. Why did you say “this is the biggest problem in this paper”? We have measured all of the ions in PM<sub>2.5</sub>, why do you conclude that “the proportions of different ions in PM<sub>2.5</sub> could not be obtained”?