

Responses to Interactive comment on “New characteristics of submicron aerosols and factor analysis of combined organic and inorganic aerosol mass spectra during winter in Beijing” by Referee #1

This manuscript reports the results from PMF analysis of an ambient AMS data collected in winter 2014 in Beijing. Six organic factors were determined through analyzing the aerosol spectra including both organic and inorganic signals. Discussions on aerosol sources and processes are made based on these results. Some comparisons with the AMS observation from winter 2013 are also discussed. This work fits well to the scope of ACP and the manuscript is overall well written. I recommend this manuscript for publication after the authors address the following comments.

We are thankful to the referee #1 for his or her comments and suggestions, which contribute to improve the quality of our paper. We have revised the manuscript accordingly. Listed below are our point-by-point responses in blue to reviewer's comments. To make a more convenient reply, we named every comment using the red and bold Arabia number (such as **1, 2, 3.....**).

1. Page 18456 – 18457, the discussions of aerosol aging based on the O/C of bulk organic aerosol is problematic. Oxidative aging is not the only reason for changing bulk O/C observed in ambient aerosol. Mixing of OA from different sources and with different degrees of oxidation can lead to O/C changes as well. For example, a decrease of O/C can be observed simply because of a larger contribution from chemically reduced POA from vehicle emissions and coal combustion, which often happens at night when temperature is usually lower and RH higher compared to daytime. The relationships observed between O/C and T (and RH) don't necessarily suggest a definitive connection between oxidative aging of OA and meteorological conditions. It is thus inappropriate to use the observed increase trend of O/C with RH to claim aqueous processes. In fact, what's the liquid water content? Water-uptake by particles is likely very low at RH \sim 45%, even for particles composed mostly of hydrophilic inorganic salts. What's the base to claim that OA aging is dominated by aqueous-phase processes when RH was higher than 45%?

Reply: We are very grateful for this valuable comment. We found these analyses are not reasonable. Therefore, this section has been deleted in the revised manuscript. However, this will not reduce the richness of the article, because we added the PMF results which focused only on OA (PMF_{OA}) and discussed more in-depth, which makes the research focus more prominent (Section 3.2).

2. In this study, particles appeared to be significantly acidic according to the charge balance between NH₄ and anions (i.e., sulfate, nitrate and chloride). The observation of large amounts of nitrate and chloride in acidic particles, however, is intriguing, as HCl and HNO₃ are both highly volatile and Cl⁻ and NO₃⁻ tend to partition into the gas phase when particles are acidic. It would be helpful that the authors elaborate on this and provides some explanation for the observation.

Reply: (1) In fact, the high contribution of anions (i.e., sulfate, nitrate and chloride) in

NR-PM₁ has also been observed in many previous studies in China, such as in winter in Beijing (Sun et al., 2014), and in summer and winter in the Yangtze River Delta region (Huang et al., 2013). According to the observational data, we have produced figures to illustrate the NR-PM₁ chemical composition in these three periods.

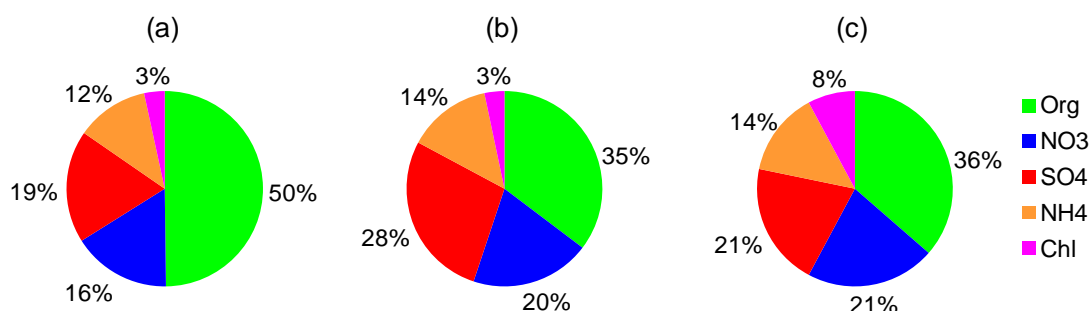


Fig. 1. The chemical composition of NR-PM₁ in (a) winter in Beijing, (b) summer and (c) winter in the Yangtze River Delta region.

It can be seen that the contributions of nitrate and chloride in winter in Beijing (16% and 3%) are very close to our results (16% and 4%), and the contributions of nitrate and chloride in summer (20% and 3%) and winter (21% and 8%) in the Yangtze River Delta region are much higher than our results. Meanwhile, the contributions of sulfate in their studies are all higher than in our study (17%). Therefore, these results further prove the rationality of the results in our study.

In addition, the strong aerosol acidity in Beijing was also reported by Sun et al. (2015) ($\text{NH}_4^+_{\text{measured}}/\text{NH}_4^+_{\text{predicted}} = 0.65$), Xu et al. (2015b) ($\text{NH}_4^+_{\text{measured}}/\text{NH}_4^+_{\text{predicted}} = 0.75$), and Chen et al. (2015) ($\text{NH}_4^+_{\text{measured}}/\text{NH}_4^+_{\text{predicted}} = 0.56$ and 0.62). The study period of Sun et al. (2015) partially overlapped with our study.

(2) This aerosol acidity calculation method is only based on the NH₄ and three other anions (i.e., sulfate, nitrate and chloride). However, the effect of metal ions and organic acids on the aerosol acidity should not be neglected in the actual atmospheric environment. Therefore, the real aerosol acidity in the atmosphere is not as strong as the calculation results in this study. However, the components that can be observed by AMS are very limited (Org, NO₃, SO₄, NH₄, and Chl), due to the principle of AMS. Therefore, the calculation results based on the AMS results should be mainly used for a preliminary understanding of aerosols, and comparison with other AMS observation results. It is inappropriate to use them to evaluate the actual acidity of aerosol in the atmosphere.

(3) The average temperature in this study was only 1.5 ± 3.4 °C. Therefore, the lower temperature is not conducive to Chl and NO₃ to partition into the gas phase.

3. In addition, it might be worthwhile to check whether correct RIE values are used for ammonium and sulfate. While the RIE for NH₄ is commonly determined during IE calibration, the RIE for sulfate is not determined and a default value of 1.2 is used for sulfate. However, previous studies found the RIE for sulfate could be quite different depending on instrument tuning. Was ammonium sulfate analyzed to determine the RIE for sulfate? If not, I suggest the authors consider doing so.

Reply: Thank you very much for the useful suggestion. In the previous observation, we used the default value of the RIE value of sulfate, as in most previous studies, e.g., the studies in

Paris (Crippa et al., 2013), the Pearl River Delta region of China (He et al., 2011; Huang et al., 2011), Changdao island (Hu et al., 2013), Beijing (Huang et al., 2010; Chen et al., 2015; Sun et al., 2015), Shanghai (Huang et al., 2012), the western Mediterranean (Minguillón et al., 2015), New York City (Sun et al., 2011), the Yangtze River delta region of China (Zhang et al., 2015), and so on. According to the suggestion of the reviewer, we determined the RIE for sulfate during the AMS calibration work several days ago. We found that the RIE for sulfate (1.21) is very close to the default value. Therefore, we believe the default value is appropriate in this study.

In addition, in order to prove the rationality of our result, we:

(1) Compared with several previous similar studies. Sun et al. (2015) conducted simultaneous real-time measurements of aerosol composition at two different heights at the same location in urban Beijing from 19 December 2013 to 2 January 2014. This research period partially overlapped with our study period. In their study, they also used the default value of 1.2 for the sulfate RIE, and the aerosol acidity (slope=0.65) was very close to our results (slope=0.68). Meanwhile, Chen et al. (2015) and Xu et al. (2015b) also used the default value of 1.2 for the sulfate and found that the $\text{NH}_4^+_{\text{measured}}/\text{NH}_4^+_{\text{predicted}} = 0.56$ and 0.75 .

(2) In the revised manuscript, we compared the AMS results with the PM_{10} mass concentration monitored using a beta-attenuation method (Metone BAM-1020, USA), the $\text{PM}_{2.5}$ mass concentration was monitored using Tapered Element Oscillating Microbalance (TEOM series 1400a, Thermo Scientific), and the particle volume variation was measured with a collocated Scanning Mobility Particle Sizer (SMPS, TSI Inc.). Comparisons revealed that the results were very close to those reported in several previous studies, further proving the correctness of our observation results (line 238-249).

4. Are there chemical differences between the nitrate associated with $\text{NO}_3\text{-OA1}$ and $\text{NO}_3\text{-OA2}$? For example, what are the $\text{NO}^+/\text{NO}_2^+$ ratios for those two factors and how do they compare to the ratio in NH_4NO_3 ? It appears that some NO^+ and NO_2^+ are associated with CCOA and HOA too, what are the $\text{NO}^+/\text{NO}_2^+$ ratios in them?

Reply: Thank you very much for the useful suggestion. The $\text{NO}^+/\text{NO}_2^+$ ratios for $\text{NO}_3\text{-OA1}$ and $\text{NO}_3\text{-OA2}$ are 2.69 and 2.21, respectively, close to the value of 2.8 for NH_4NO_3 determined in the AMS calibration. They were also in the range of 1.5 to 2.9, reported in some previous studies (Farmer et al., 2010; Fry et al., 2009; Bruns et al., 2010; Hao et al., 2014). Meanwhile, the ratio for CCOA is also at a low level (2.03). These factors show the characteristics of inorganic nitrate. However, the ratios for HOA (12.5) and COA (14.5) are much higher than that in the $\text{NO}_3\text{-OA1}$ and $\text{NO}_3\text{-OA2}$ and CCOA, which corresponding to the ratio range of 10–15 measured for organic nitrate in laboratory chamber experiments (Fry et al., 2009; Bruns et al., 2010; Hao et al., 2014). Thus, the nitrate which distributed in these factors is corresponding to the organic nitrate. This discussion has been added in the manuscript now (line 324-328, 444-448). Meanwhile, these results also prove the necessity of the PMF analysis, which focused on the organic and inorganic species HRMS.

5. What's the logic of using the distribution of the 6 OA factors on the f44 - f43 space or the VK diagram to infer the aging pathways of OA as discussed on page 18554 – 18555?

Reply: These two methods were discussed in detail by Ng et al. (2010) and Heald et al. (2010),

respectively. Furthermore, they were used to investigate the evolution of eight OA factors (SO₄-OA, NO₃-OA, HOA, COA, NOA, LO-OOA, MO-OOA, LV-OOA) by Sun et al. (2012). (1) f44 - f43: The intensities of m/z 44 (mostly CO₂⁺) and 43 (mostly C₂H₃O⁺ or C₃H₇⁺) are important for classifying OA factors. They are an important indicator for judging the oxidation of OA factors. For example, LV-OOA has been described as aged OOA, with spectra dominated by mass fragment CO₂⁺ at m/z 44, and SV-OOA, described as “fresh” OOA with an intense signal at C₂H₃O⁺ at m/z 43 as well. Mass fragment CO₂⁺ has been considered a marker ion for organic acids in OA, as it is known to form from the thermal decarboxylation of many different oxo-, di-, and polycarboxylic acids (Alfarra, 2004; Aiken et al., 2007; Takegawa et al., 2007; Duplissy et al., 2011). Fragment ion C₂H₃O⁺, conversely, has been hypothesized to form from non-acid oxygen-containing organic compounds. Since m/z 43 and 44 are the dominant ions in SV- and LV-OOA spectra and represent different functionalities, Ng et al. (2010) plotted f44 vs. f43 for all OOA spectra from different sites, where f44 and f43 are the ratios of m/z 44 and m/z 43 to the total OA signal in the spectrum, respectively. They found that the OOA components clustered into a triangular region with wide variability across f43 at low values of f44 that narrows as f44 increases. As a consequence, LV-OOA data tend to group in the top half of the “triangle plot” and SV-OOA in the lower half (Chhabra et al., 2011). Therefore, a detailed comparison of these mass fragments from observation sites may yield some insights regarding the dynamic evolution of OA factors in the atmosphere. This method has been widely used to investigate the evolution of OOA factors (Heringa et al., 2012; Ng et al., 2010; Zhang et al., 2011) and all PMF factors (Mohr et al., 2011; Sun et al., 2012).

(2) VK diagram: The aging of OA is generally characterized by an increase in O/C and a decrease in H/C. The different aging mechanisms of OA follow different slopes. The bulk composition of OA from a variety of environments (laboratory and field) occupies a narrow range in the space of a Van Krevelen diagram (H:C versus O:C), characterized by a slope of ~ -1. The data show that atmospheric aging, involving processes such as volatilization, oxidation, mixing of air masses or condensation of further products, is consistent with movement along this line, producing a more oxidized aerosol. This space can be used to illustrate how reactions involving the addition of functional groups fall along straight lines. For example, the replacement of an aliphatic carbon (-CH₂-) with a carbonyl group (-C(=O)-) implies a loss of 2 hydrogens and a gain of 1 oxygen, and thus a slope of -2 in the Van Krevelen diagram. Conversely, the replacement of a hydrogen with an alcohol group (-OH) involves an increase in oxygen but no change in hydrogen, and therefore is a horizontal line in Van Krevelen space. An intermediate slope of -1 is produced by the simultaneous addition of both functional groups, forming a hydroxycarbonyl or carboxylic acid. Organic atmospheric functionalization reactions, including, but not limited to those shown here, generally involve changes not only to O:C but also to H:C. This method was also used by Hu et al. (2013), Sun et al. (2012), Ng et al. (2011) and Xu et al. (2015a).

Detailed comments:

6. Last paragraph on page 18539, a comprehensive review of the PMF analysis of AMS data is given in “Zhang, Q., Jimenez, J. L., Canagaratna, M., Ng, N. L., Ulbrich, I., Worsnop, D., and Sun, Y. L.: Understanding organic aerosols via factor analysis of aerosol mass

spectrometry: A review, *Analytical and Bioanalytical Chemistry*, 401, 3045-3067, 10.1007/s00216-011-5355-y, 2011.”

Reply: [We have cited this reference \(line 82, 88, and 886-888\).](#)

7. Line 28, page 18550, change ug m-3 to um.

Reply: [It has been changed \(line 383\).](#)

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