Atmospheric
Chemistry
and Physics
Discussions

Open Access

Interactive comment on "New characteristics of submicron aerosols and factor analysis of combined organic and inorganic aerosol mass spectra during winter in Beijing" *by* J. K. Zhang et al.

Anonymous Referee #2

Received and published: 31 July 2015

This paper presents AMS measurements in Beijing during January 2014 and compares the results obtained with a previous study from the same group during January 2013. Results are analyzed using positive matrix factorization, where both organic and inorganic species are included. The results are very similar to those obtained in previous studies at the same location. The authors claim that the "novel" approach used including both organic and inorganic species enhances the resolving power of PMF. However, not only I do not agree with their claim about the novelty of the work, but I also strongly believe that such conclusions cannot be drawn, without comparing the results obtained

to those from a more traditional PMF where only organic fragments are included, such conclusions. This is a great limitation of the paper. In general, the authors did a poor job in validating their PMF results, especially in the lack of external data supporting their interpretations. Note that the study is limited to AMS measurements only. Despite such limitations, the authors make several bold statements about the chemical mechanisms via which secondary species are formed, sources' geographical origins and abatement strategies, which are not supported by their data and that are only based on speculations. Some technical issues regarding AMS data analysis can also be pointed out (e.g. CE determination, RIE determination). The authors mainly cite their own work and omit some important citations from other groups (e.g. from pku university, Chinese Academy of Sciences...). In my opinion, this is not transparent. Accordingly, I do not support the publication of this work under its current form. Specific comments – main text: 0/ title: I do not see the new characteristics. The results obtained are very similar to those presented in previous studies, at the same location.

1/ Page 18538, line 8: This is not the first time that inorganic and organic mass spectra are put together in PMF and I do not consider that this is a revolutionary advancement in the field to justify the publication of this study.

2/ Page 18538, line 19: I do not see any solid result to support such a bold statement!

3/ Page 18539, line 10; "air quality index > 200": Either define or remove.

4/ Page 18539, line 22; "After combining the organic mass fractions observed by the AMS": Not clear.

5/ Page 18540, line 1-2: The sentence does not make sense.

6/ Page 18540, line 5: What is the intrinsic relation between organic and inorganic species? They may have common sources, but their precursors, formation rates, partitioning properties and sinks are completely different.

7/ Page 18540, line 17: This is inaccurate; Crippa et al., could resolve the MOA, with-

out the addition of the inorganic fraction. They include the latter to enable the SO4 apportionment between marine and continental sources.

8/ Page 18540, line 22: Again here I do not see the novelty of the approach used and the science presented. You mention that no work before you had applied PMF to OA and inorganic aerosol mass spectra : I am sure that this is only a slip and you are not aware of the work of Huang et al., 2014.

9/ Page 18542, line 4: DeCarlo et al. (2006) is not a review.

10/ Page 18542, line 8: 22.5s is very long, what was the reason for that choice? (it only worsen your data quality).

11/ Page 18542, line 12: Did you determine the NH4 and SO4 RIEs? (Apparently not, see below).

12/ Page 18543, line 3: Having a constant bias in Figure S3 - i.e. a constantly acidic aerosol) - is seriously iffy: To make any conclusion about the acidity of your aerosol you have to determine the RIE of sulfate. 1.2 is a generic number, but we have observed RIEs as low as 0.8 or as high as 1.5. In addition, a key assumption here is that Cl is bound to NH4; there is no way this can be proven... This nonsensical parametrization is in my opinion complicating your mass determination, as it won't matter whether you use a CE=0.45 or a CE=1-0.73*(NH4/NH4, predicted)=1-0.73*0.68=0.5. An indication that your total mass determination (or CE) is not completely off is the comparison between the AMS and Metone results. Now, there could be compensating errors, as for example the use of a wrong SO4 RIE or a high contribution of refractory species (e.g. black carbon) or particle bound water not measured by the AMS; therefore you should be careful when providing quantitative numbers. In this regards, where there any black carbon/elemental carbon measurements? If yes, why did the authors omit any discussion about it? You know there are instruments other than the AMS. Also, did you have any SMPS measurements? This would help constraining the CE.

13/ Page 18543, line 14-15: I am not convinced that this can be generalized.

14/ Page 18545, line 1-3: This is very vague! Please explain. I would expect the mass determined with the AMS to be lower, for the same reasons I have mentioned above (a lens cutoff lower than 1 μm, the presence of particle bound water and refractory species).

15/ Page 18545, line 4-7: "Figures 1d and e compare the composition of NR-PM1 between January 2013 and January 5 2014. The contribution of organics in January 2014 accounted for 54% of the total mass, which was slightly higher than in January 2013." Then you say "In contrast, the contribution of total inorganic species was reduced." Redundancy. . .

16/ Page 18545, line 7: How subtle is that? Please specify.

17/ Page 18545, line 20: "This implies that there was a striking increase in the oxidation of OA in January 2014". This contradicts your previous statement in the same page, that secondary processes were more important during more extreme haze conditions in 2013.

18/ Page 18545, line 22: compared to O3, OH is much more efficient.

19/ Page 18545, line 22: A similar variability between increased temperature and SOA production is only correlation and not causation. Aging does not occur through heat!

20/ Page 18545, line 24: use the present tense: shows instead of showed. In general the English/the grammar need polishing.

21/ Page 18545, line 26: You are considering changes in the composition, in particular O/C, and photochemical extent against supposedly independent variables (e.g. temperature as a surrogate of photochemical aging, or RH). However, these variables are not independent and I think that much of this is correlation but not causation. Therefore this analysis cannot be used to determine the mechanism by which OA ages. I give some examples. At higher temperature, I would expect less contribution from combus-

tion sources and hence higher OOA contribution and O/C ratios. The analyses you are presenting do not take into account any change in primary emission contribution, but your conclusion is that at higher temperature aging is more important. A lot of the statements are not fully justified and need toning down. Haze events are often associated with higher RH, where secondary processes are more important (due to stagnation and higher cloud processing). That does not mean that cloud processing is a major contributor to SOA as you claimed. Are O/C ratios of SOA from aqueous phase chemistry and from homogeneous photo-chemistry the same? The argumentation you are presenting is based on such assumption. Can you validate this assumption?

22/ Page 18548, line 24: Is that normalized to OA in NO3-OA factors (right) or to the total spectrum (wrong)?

23/ Page 18549: It would be useful to also normalize the contribution to OA, for a comparison with previous source apportionment data.

24/ Page 18549, line 12: From where did you obtain the time dependence of the equilibrium constant? This is not shown here and not explained. Kp is dependent on temperature and RH, but the formation of NH4NO3 is also dependent on the available NH4. In this regards, the formation of NH4NO3 is not at all favorable in acidic conditions with no gas-phase NH4 available (maybe check Seinfeld and Pandis 2008), while this is what you are suggesting (recheck your RIE)...

25/ Page 18549: The interpretation of the nitrate factors is very speculative/dubious to say the least. You are suggesting that NO3-OA1 formed via the N2O5 hydrolysis follows the expected portioning behavior of nitric acid. Whether HNO3 is formed by the heterogeneous hydrolysis of N2O5 or by the reaction of NO2+OH, its partitioning into the particle phase is driven by temperature, RH and the availability of NH4 (particle acidity). Further, I would not expect that the nitrate resulting from the 2 processes have distinguishable mass spectral profiles to be separated in PMF. Therefore, this separation is most-likely driven by the organic mass spectra. As you have mentioned

Sun et al. (2014) have resolved similar factors without including the inorganic ions, but here it is not clear how did the inorganics help in resolving the factors. For the case of the nitrate factors, you may check the neutrality in these spectra, which would give you an indication whether some of the nitrate signal detected is not related to ammonium nitrate (may be organic nitrate or some other primary salts: NaNO3 or KNO3). You can also look at the ratio of NO/NO2 compared to that from nebulized NH4NO3. I believe in general that the organic mass spectra helped the resolution of several inorganic containing profiles and not vise-versa. But, to convince me you would need to run an OA-only PMF.

26/ Page 18550: The discussion about aerosol acidity and nitrate formation is all biased by the presence of organic-nitrate, other nitrate salts from combustion, and the SO4 RIE determination....

27/ Page 18551, line 13-17: If Sun et al. (2014) were able to distinguish the same factors than here using OA spectra only, why was that not possible in the current study. In general, without a comparison between the OA-only PMF and all-species-PMF, the reader does not get how this inclusion affects the capability of PMF to resolve additional sources.

28/ Page 18553, line 21: I did not understand you expect that all primary emissions to have the same composition and the difference in their O/C ratio is only due to aging?

29/ Page 18554, line 1-3: That cannot be assessed because we do not see how OA-only-PMF performs.

30/ Page 18555, line 7-11: This is not as straightforward as presented here. Caution has to be taken; consult Chhabbra et al. (2011-ACP) and El Haddad et al. (2013-AE).

31/ Page 18558, line 10-20: What is considered as a regional scale? Is it 20-40km or greater than 100Km? Your diurnals seem to suggest that most of the sources are rather local or at least close; it depends on the wind speed, but for winter winds in china

Interactive
Comment

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

below 10Km h-1, it needs at least 5h to transport primary emissions 50km away from the sampling site, e.g. in the Hebei region. This has to be clarified. Specific comments – Supplement: You claim that the factor extracted is related to coal because you expect that coal emissions are important. If you already know the important sources, then why take the trouble to perform the source apportionment. You cite the studies that extracted a coal burning factor in Beijing, but this shows on the one hand that what you did in the current study is not new and on the other hand the studies cited are all from your group, which do not really support your case. In general, as I have mentioned above, it appears that you did not examine and validate systematically the PMF results. This validation should be based on a systematic examination of the mass spectral profiles, the diurnals, the correlation between tracer and factor time-series. The study seriously lacks external data to support factor identification, all the more since the inorganic species were included in PMF. Amongst the 6 factors identified, the only factor supported by external data is traffic. The CCOA mass spectrum looks like that of BBOA, and additional data are needed to support your assignment. For the secondary factors, it would be more appropriate to compare a traditional organic only PMF to the all-species-PMF presented here, as in the case of organic only PMF more species are available for validation. Also, please remove the following statement: "Most importantly, the 6-factor solution was in agreement with the actual situation in Beijing".

———————————————————

Interactive comment on Atmos. Chem. Phys. Discuss., 15, 18537, 2015.

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper