Referee comment

Chemical characterization of fine particular matter in Changzhou, China and source apportionment with offline aerosol mass spectrometry

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Anonymous referee #2

General comments

This manuscript reports results obtained during a long-term measurement campaign performed at Changzhou, China. The authors sampled $PM_{2.5}$ particles on filters during one year (one month per season) and used a wide range of off-line analytical techniques to determine the concentration and chemical composition of these samples.

This is a long and important effort in terms of sampling, off-line analysis and data treatment. Results reported in this manuscript will be of interest for the readers of *Atmospheric Chemistry and Physics*. I recommend its final publication after the authors address the following comments.

Specific comments

1) The main issue of this manuscript is the absence of discussion on the uncertainty of the results. Given that the authors used a large set of analytical techniques, they should present their uncertainties in their respective sub-section under 2.2 "Chemical analysis". This is particularly important for a few parameters which are calculated using results from two instruments, such as the concentration of water soluble organic aerosols (WSOA), which is obtained from the TOC analyzer and the OM/OC ratio of the SP-AMS.

2) Section 2.1 "Sampling site and $PM_{2.5}$ collection": the authors need to mention here the artifacts related to the filter samplings, in particular the evaporation of semi-volatile compounds during the sampling. This is particularly important for some results presented later, such as the NO_3^-/SO_4^{2-} ratio. Indeed, if these species are present under the form of ammonium nitrate and ammonium sulfate (as shown in section 3.2), ammonium nitrate will evaporate faster than ammonium sulfate during the sampling. Therefore, the concentrations of nitrate correspond to a lower limit, the real concentrations should be higher, and the real NO_3^-/SO_4^{2-} ratios should also be higher. Another artifact concerns the adsorption of gases, such as volatile organic compounds (VOCs), onto the sampling media and collected particles, which can have an impact on the concentration of particle-bound polycyclic aromatic hydrocarbons (PAHs).

3) Section 2.1 "Sampling site and $PM_{2.5}$ collection": according to the wind rose plots presented in Fig. S1, the sampling site was under the influence of different air masses, depending on the season. This important information is not discussed in the section 3 "Results and discussion" and the corresponding sub-sections. Did the authors perform a back trajectory analysis to check where the air masses come from during each sampling period?

4) Section 2.2.5 “Offline SP-AMS analysis”: it would be interesting if the authors explain here the advantages to use the SP-AMS for off-line analysis of filter samples. This kind of analysis presents several problems compared to on-line measurements: a) it has a much lower time resolution (20 hours in this study, instead of a few minutes), b) the total concentrations and size distributions of the species cannot be directly measured (given that the water extracts must be atomized), and c) it introduces artifacts related to the filter sampling. So what are the advantages of using that instrument for off-line analysis?

5) Section 2.4 “Source apportionment of WSOA”: the authors should say a few words on the robustness of this PMF analysis, given that the dataset contains only 69 samples (67 if the authors discarded two outliers) and corresponds to 20-hours averaged samples.

6) Lines 369-372: in addition to cations not measured by ion chromatography, a NH_4^+ measured/NH_4^+ predicted of 0.75 in winter can also simply be due to the presence of acids.

7) Lines 380-383: in summer, the high temperature may lead to a faster evaporation (not dissociation) of nitrate during the filter sampling. This may explain the lower NO_3^-/SO_4^{2-} ratio in summer.

8) Lines 389-391: the authors mention that the sulfur oxidation ratio was higher in summer. However, according to Fig. 6c, the difference with the other seasons does not seem significant.

9) Lines 538-542: it is surprising to notice that the O/C ratio of organics remained almost constant during the four seasons (Fig. 2), while we could expect higher values in summer due to increased photochemical activities. Can the authors say a few words on this in the manuscript? Among all the results presented in this manuscript (OC/EC ratio, etc.), only a higher sulfur oxidation ratio in summer seems to show increased photochemical activities during that period.

Technical comments

10) Several correlation coefficients are reported throughout the manuscript. Sometimes, the authors use the Pearson’s coefficient r, and sometimes the r^2. It will be better to be consistent and use systematically the same correlation coefficient, either r or r^2.

11) When at least two references are given in parentheses, please add a space after the semicolons.

12) Title (also in the supplementary material): “Chemical characterization of fine ~~particular~~ particulate matter”.

13) Line 24: “the fine ~~particular~~ particulate matter ($PM_{2.5}$) samples”.

14) Line 103: “short-term” is quite vague here. The typical duration of field campaigns with the AMS is approximately one month.

15) Lines 183 and 446: the authors may mention in the title of these two sub-sections that they are talking about particle-bound PAHs, not about gas-phase PAHs.

16) Line 276: by which factor were ions with S/N ratios between 0.2 and 2 downweighed?

17) Line 301: “Previous studies ~~shows~~ showed that low”.

18) Line 363: actually, the NH_4^+ measured/NH_4^+ predicted ratio was first presented by Zhang et al. (2007), and used in tens of papers afterwards, Young et al. (2016) being one of them. Therefore, I would suggest to replace this reference.

19) Lines 649-650: “and Pollution Control (KHK1409)~~,~~. We would”.

20) Figure 7: it would be important to include error bars corresponding to the standard deviations. This is particularly important for the Zn concentration in winter: is this high value due to 1-2 outliers, or do all the samples have a high value?

21) Figure 9: please scale the x-axes of the two panels the same way (either *m/z* 10-100 or 10-120).

References

Young, D. E., Kim, H., Parworth, C., Zhou, S., Zhang, X., Cappa, C. D., Seco, R., Kim, S., and Zhang, Q.: Influences of emission sources and meteorology on aerosol chemistry in a polluted urban environment: results from DISCOVER-AQ California, Atmos. Chem. Phys., 16, 5427-5451, 10.5194/acp-16-5427-2016, 2016.

Zhang, Q., Jimenez, J. L., Worsnop, D. R., and Canagaratna, M.: A case study of urban particle acidity and its influence on secondary organic aerosol, Environ. Sci. Technol., 41, 3213-3219, 10.1021/es061812j, 2007.