Atmos. Chem. Phys. Discuss., 14, C4922–C4934, 2014
www.atmos-chem-phys-discuss.net/14/C4922/2014/

Atmospheric Chemistry and Physics Discussions

Interactive comment on “Insights into characteristics, sources and evolution of submicron aerosols during harvest seasons in Yangtze River Delta (YRD) region, China” *by* Y. J. Zhang et al.

Anonymous Referee #3

Received and published: 15 July 2014

In their manuscript “Insights into characteristics, sources and evolution of submicron aerosols during harvest seasons in Yangtze River Delta (YRD) region, China” Zhang and coworkers present results from two two-week measurement periods in summer and fall 2013 using an Aerodyne ACSM for non-refractory sub-micrometer aerosol components together with a MARGA to measure potassium ions in the aerosol and additional instruments to measure PM1 and black carbon in PM2.5. Furthermore gas analyzers to measure CO, NO2 and O3 were also deployed as well as a met station. The measurements were performed on top of a not further specified 6-story building in urban Nanjing (more than 8 Million inhabitants) during the main periods of wheat harvest (summer) and rice harvest (autumn).

Time series of PM1 components as well as meteorological factors were presented and average values for the two intervals were determined. Diurnal variations of these data were presented and partially discussed. Using PMF three different types of organic aerosol, i.e. HOA, OOA, and BBOA, were extracted from the ACSM data and their time series were compared to other species time series and discussed. The contribution especially of the BBOA organics fraction to total PM1 with a special focus on very polluted days is discussed in order to determine the biomass burning contribution to air quality. This analysis was also used to determine a simplified method to determine BBOA concentrations from the marker peak m/z 60 and total organics signal. Briefly, information on oxidation processes is attempted to be extracted from the data and finally with the help of HYSPLIT back trajectories the contributions from different regions around the sampling site are investigated.

Generally the content of the paper is suited for ACP and the paper is well written with few linguistic weaknesses. As detailed below there are a few passages that are hard to understand and should be reworded. For several of the Figures it is hard to see the information, e.g. because different shapes of symbols cannot be distinguished or because information is printed on top of each other. The two major weaknesses of the manuscript, however, are the missing focus of the work and many conclusions that are either not sufficiently supported by the data or drawn from pretended behavior of the data that is not in agreement with the data presented in the figures (see detailed comments below). Data from a set of aerosol and trace gas measurements operated over two relatively short time intervals are presented together with a very broad analysis of these data. For a real characterization of the aerosol or of the sources or of the transformation both, the data and the analysis are not sufficiently deep. I have the impression that everything that can be done with this data set has been done and is presented in this paper without a real focus of the work. As a result the paper is rather long with many figures (13 figures in the main text and additional 5 figures in the supplement that are also referenced in the text; many of the figures with two or multiple panels) and at the same time only gives a rather limited depth of information. Here I agree with the first reviewer that not much new information is provided by this manuscript.

I also agree with the first reviewer that the “poor man’s PMF” method, the method to derive information on different types of organics (e.g. on BBOA) without the need to perform a full PMF analysis, is a very interesting approach. However, this approach is not new. Weimer et al. submitted a comparable approach to ES&T in 2008 (Dissertation S. Weimer, ETH Zürich, 2008). In 2009 Aiken et al. (ACP) presented also such a method to estimate BBOA and other organic particle types concentrations which was also used in Ng et al. 2011 (ES&T) or Lee at al., 2010 (AS&T). While this approach allows a good approximation of BBOA concentrations without the need to perform PMF it has a major limitation: For each data set the factors used to convert the m/z 60 signal into a BBOA concentration are different. Since these factors are determined using the PMF results this method cannot be used to determine BBOA concentrations on-line as stated by the authors here. Since there are already several attempts to determine BBOA from the marker peak at m/z 60 I think a more thorough analysis and discussion of the variability of the factors used for this calculation would be appropriate in order to develop this approach into the direction of a real on-line BBOA estimate.

Taking this and the many other comments below into account I cannot suggest publication of this manuscript in ACP before major revisions that result in a more focused and deeper analysis and presentation of the interesting data. For example focusing on the identification of the contribution of the harvest-related emissions to local air quality with more in-depth apportionment to the sources together with a discussion of the limitations of this apportionment would provide valuable information on this special type of aerosol and its impact on air quality in this area. For this purpose also external information on the sources should be included and presented. Also information on the

Full Screen / Esc
Printer-friendly Version
Interactive Discussion
Discussion Paper

typical aerosol during the times between the harvest periods could be used to identify and distinguish the harvest contribution. At the same time the manuscript would gain if the authors avoid conclusions that are not properly supported by the data. The detailed comments below are partially intended to make this clearer.

Detailed comments:

P9111L16-17: BBOA mass concentrations increase with increasing PM1 for large mass loadings. However, this does not imply that BBOA plays a “dominate” (better: “dominant”) role in high PM pollution. According to the data presented in this paper the BBOA contribution is in the order of only 20-25% even for these large PM concentrations. This is not a dominant contribution.

P9111L18-20: The good correlation between the K+ ion and BBOA concentrations can make K+ a good tracer for wheat and rice straw burning. However, before you can claim that it “is” a good tracer you need to show that there are no other relevant sources for this ion.

P9111L2527: This sentence is not specific at all and does not really contain any relevant information.

P9112L11-14: This sentence is hard to understand – please reword.

P9112L22-24: PMF is used frequently in the AMS/ACSM community. Other groups also use other types of source apportionment approaches.

P9112L25: To make clearer what you want to say I suggest changing “. . . can only be employed to analyze OA datasets (. . .), but cannot be easily utilized in real-time . . .” into “. . . can only be employed to analyze OA datasets a posteriori (. . .), but cannot be easily utilized in real-time . . .”

P9113L7: Replace “appointments” by “apportionment”

P9113L11: Replace “predict” by “determine”

P9113L14-24: This text is rather unclear. The information is partially hard or not to understand. Please reword.

P9113L25-26: What do you want to say with this sentence?

P9114L11-13: This is not true. The BBOA mass concentrations have not been determined on-line based on the m/z 60 mass concentration. Before this calculation can be done first PMF has to be performed in order to obtain the conversion factors for this calculation.

P9112-P9114: In the introduction some detailed information should be given on the sources that are the focus of this investigation. What is typically burned during harvest season? Who burns it? How is it burned? Is there a typical time when material is burned? How dry is the material typically?

P9114L19-26: Unfortunately this section does not provide a good idea of the measurement site. According to the text it is located in a city of more than 8 million which is almost a megacity. Therefore, enormous influence from traffic, residential or industrial activities on air quality can be expected. What is the distance to such sources? What is the influence by such sources? How far are biomass burning sources away? How large is the expected transport time from such sources to the measurement site? If there are many restaurants in the vicinity of the sampling site as stated I wonder why not cooking aerosol is found and identified in PMF. During other field campaigns in cities it has been identified as a major fraction (>20%) of the organic aerosol.

P9115L14,17: It is unfortunate that the MARGA and the aethalometer were used with a PM2.5 cyclone. Therefore, it would be desirable to get an idea on the fraction of K+ and BC that is expected in the PM1-PM2.5 size range.

P9115L24ff: What exactly are the “fire products” used here? What are the limitations of these products – e.g. minimum size of fires, time resolution?

P9116ff: Relative ionization efficiencies (RIEs) and collection efficiencies (CEs) are discussed here. Can you also provide the RIE for organics? Can you provide some information on ionization efficiency (IE) calibrations? How often, how, where have they been performed? How reproducible were the results?

P9117L15ff: In Figure 1 time series of many meteorological factors and PM1 components are shown. Most of the time series are not discussed. No information is taken from the temporal evolution of all these data, e.g. determination of meteorological situations, typical temporal trends of variables, etc. What is the point of showing the time series if the data are not used to extract information from them?

P9118L12-14: What are the reasons for these sharp peaks of very high mass concentrations? There are in total 3 such peaks during the 4 weeks of measurement. Can they be associated with certain sources in close proximity? How long do they last? Should they be used to calculate correlations or do they represent "contaminated" data?

P9118L22ff: How are average wind directions calculated? According to Figure S2 in autumn the majority of wind directions were from north (345°-15°). This is not at all reflected in the average diurnal wind direction patterns in Figure 2. According to this the typical wind was from south (180°), which according to Figure S2 almost never occurred. Also the statement that the diurnal variations of wind directions are similar for the two periods seems therefore not correct. When looking at Figure S2 one sees clearly that the wind patterns are very different during the two periods. For other variables there are also clear differences in the diurnal variations. Even though the general temporal trends are similar partially strong differences in the heights of peaks during certain times of the day occur.

P9119L6-8: Are the three peaks in the SO4 diurnal pattern significant? With only 2 weeks of data I would expect such small peaks to be generated by fluctuations of concentrations. Is it realistic to assume that the morning peak is generated by sulfur-containing fuel? What is the fuel sulfur content in that region?

P9119L15: The "two distinct peaks" in the NO3 diurnal pattern looks more like one

Full Screen / Esc
Printer-friendly Version
Interactive Discussion
Discussion Paper

peak during night. The “minor peak” mentioned in line 23 is not visible to me – is it significant?

P9118L20-P9120L4: To explain the diurnal patterns of the different PM components only potential sources are discussed. The effect of boundary layer height is completely ignored. Please include this into the discussion.

P9120L7: PMF was used to separate three different types of organic aerosol: HOA, BBOA and OOA. This is a bit disappointing, especially since the measurements were performed in an urban area with multiple restaurants around the measurement site. It would be nice if HOA could be separated into a traffic-related HOA and a cooking-related COA.

P9120L11-12: The average absolute BBOA contribution to the PM1 aerosol is 50% larger in autumn compared to summer. I would not call this “similar” – especially if much smaller differences are used to draw conclusions further down the text.

P9120L24: Add “used” between “can be” and “as a diagnostics”

P9121L22: Should “consistent” not be “correlated”?

P9121L23: According to Figure 4 r2 is 0.93, not 0.96.

P9122L5: What are the “BB activities” that are mentioned here? Can you specify this further?

P9121-9122: It would be interesting to see whether there is a wind direction dependence of the concentrations of the different OA types.

P9122L14-15: “OOA . . . is one of the most important secondary sources of . . .”. OOA is not a “source”, it is a type of organic aerosol.

P9123L2-4: Since in Figure 5 only averages for the time intervals are shown I would not call this “dynamic variations”. This term would be more appropriate for time series of data. I would also not call these differences “strong”. For the visibility no significant difference is observed (within the error ranges) and for the other variables no error bars are presented. I would expect these differences also not to be significant. For SO4, NH3 and Chl no difference can be seen in the data. There seems to be a NO3 and NH4 increase in the BB-events compared to the non-BB times as well as an increase in HOA and OOA. Can you comment on this? Do you have an explanation for this?

P9123L15: The “value of 11.9 km” does not agree with the bar in Figure 5a.

P9123L22-25: Why do the secondary species concentrations increase linearly with increasing PM1 concentrations? From my point of view if this relationship is significant this would mean that there are either no local sources (in an almost-megacity) or the concentration of species from local sources increases exactly as the concentrations of secondary species.

P9123L27-28: The authors state that BC does not show a clear relationship with PM1. According to Figure 6 BC concentrations increase in summer about as linearly as the secondary species with increasing PM1.

P9123L20-P9124L27: There is a long discussion on the variations of individual species concentrations as a function of total PM1 concentration. All kinds of features in the graphs in Figure 6 are interpreted. Taking into account that all the graphs in Figure 6 are strongly influenced by the data points at large concentrations of PM1 (e.g. PM1 above 50 μg/m3) and that this PM1 concentration range is often discussed in this paragraph one has to recognize that there are only 3 very short time intervals during the 2x2 weeks of measurement (see Figure 1c) where such concentrations are reached. Therefore all these discussions are based on only a handful of data points and are very likely not significant at all.

P9124L15-17: I do not agree with the statement “. . . the results suggest that BBOA plays a key role in causing the highest PM pollution during the harvest seasons, whereas the role of secondary species is less significant.” For the largest PM1 concentrations the fraction of BBOA is only about 20%. So biomass burning is only one out of several sources causing this high PM concentrations. In addition the inorganic secondary species NO3, SO4 and NH4 together have a contribution of 40-45% to total PM1. This is definitely not “less significant” than BBOA!

P9124L20-22: The authors state: “. . . when the mass fraction of OA is >70%, the POA mass concentration reaches ∼100 μg/m3, while SOA is generally below ∼10 μg/m3.” How is this possible? According to Figure 1 there are only 3 very short events with PM>100 μg/m3. According to Figure 6 the POA mass fraction for PM > 100 μg/m3 is about 25%. With maximum concentrations of about 145 μg/m3 OA this is about 35 μg/m3 (and not about 100 μg/m3)! In addition according to Figure 6 for PM>100 μg/m3 SOA (OOA) is about 20-25 μg/m3 (and not below 10 μg/m3). The statement is probably only correct for individual single data points and therefore probably not really significant.

P9124L28 and others: POA should not be identified with HOA, COA and BBOA; and SOA should not be identified with OOA. Likely most of the PMF-generated organic aerosol types are associated with either POA or SOA, however identifying them with primary or secondary aerosol is not sound since this cannot be proved with AMS data. There has been a long and intense discussion in the early days of AMS organics analysis on this issue, which needs no repetition.

P9125L1-4: During autumn harvest POA loadings are about 2 times higher than during summer harvest. The authors explain this with the amount of fire sites around urban Nanjing. This explanation is hard to believe when looking at Figure S1. During autumn the number of fires shown in the Figure and also the number of fires in the Nanjing area is much smaller than during summer. Is there a potential influence by lower boundary layer height in autumn?

P9125L5-17: During times of high BBOA concentrations also SOA and SPM is increased. What is the reason for this? Are there different sources that cause high concentrations by coincidence? Is this a wind direction effect? Is the SOA from precursors that are co-emitted by the fires?

P9125L20-21: Is f60 (= m/z60 / total organics) or m60 (= signal at m/z 60) a marker for BBOA? In the formulae used here and in other studies m60 is used to calculate the BBOA concentration. In the next sentence here f60 is used. This should be handled more consistently or at least the difference should be made clear.

P9125L22-23: The background level of f60 was determined for non-BB periods. What are "non-BB periods"? From a later section of the manuscript it becomes apparent that these are periods between the two 2-week measurement periods. However, this is rather unclear. Explain and introduce these measurements in an earlier section of the manuscript. Additionally: how do you know that during these periods there was no BB-related aerosol in the air?

P9125L27: There are different slopes for the correlations between Delta-60 and BBOA. What does this mean? Can you discuss the possible reason for this and its implications. If this slope is not known a priori, a real on-line calculation of BBOA seems not feasible.

P9126L8-11: How is the information in Figure 10 different from that in Figure 9?

P9126L16: I suggest replacing ". . . overall mass concentration and fraction of OOA and .." by ". . . overall mass concentration of OOA and its fraction of OA and . . ."

P9126L20-22: Please reword. This sentence is hard to understand.

P9126L22-24: When looking at Figure 11b, I do not think this "linear relationship" is significant.

P9127L4-5: Also the "small peak" at 30 μg/m3 – 80 μg/m3 is not really significant.

P9127L8-12: This conclusion might be right, but how do the data suggest this process?

P9127L13-24: This paragraph is hard to understand. Please reword.

P9127L15-16: The degree of OA aging might be affected by atmospheric photochemical activity. Does this make sense? While Ox describes the actual level of photochemical activity the f44/f43 ratio describes the oxidation level of the aerosol which is the result of the oxidation during the history of the particles.

P9127L25-P9128L2: What are the "BB campaigns"? What is the "photochemical activity campaign"? The fraction of BBOA in total OA decreases with increasing oxidation degree of OA. Is this a result of a transformation process as suggested here – or does this just reflect the different mixing of OOA and BBOA in different air masses? The same comment is also true for the rest of this paragraph.

P9128L10-11: I do not see how this is the consequence of the previous sentence. The logical cause-effect relationship is missing.

P9128L23-26: According to the text there are high BBOA contributions in the air masses of group 3 during summer and autumn. From Figure 13 I can see the large contributions for BBOA from air mass group 3 in autumn, but not in summer. In addition the authors state that this is "consistent with the fire location distributions around this sampling site". For the summer field campaign back trajectory group 3 is from north to north-west. This is indeed in agreement with a large number and density of fires according to Figure S1a. However, for this trajectory group no increased BBOA fraction is observed (Figure 13a). For the autumn field campaign trajectory group 3 is from SE. According to Figure S1b there is no large number or concentration of fires in this direction during this time. The same is true for the direction of group 4 trajectories, for which also an increased BBOA fraction is observed according to Figure 13b.

P9128L28-P9129L5: In the plots of Figure S5 I do not see an increase of BBOA and Chl for greater wind speeds. In addition, what do you mean with "suggesting a vital role of the BB campaign around urban Nanjing in the BB pollution."? Finally, how do high BBOA and Chl concentrations associated with wind speeds of $\sim$2 m/s denote the dominant role of local burning events around Nanjing? I do not see how this provides a strong basis for this conclusion. In addition I do not see this association of high BBOA and Chl concentrations with wind speeds of ∼2 m/s.

P9129L6-8: Again I cannot agree with the statement and the conclusion. According to Figure 13 HOA and BC are not larger for group 2 and 4 compared to the other groups in summer. In autumn HOA and may be BC is larger for group 2 but not for group 4. In addition according to Figure 13 both, group 2 and group 4 back trajectories arrive at the measurement site from east to northeast during both measurement periods and not from north as stated by the authors.

P9129L14-16: Again it is hard to follow the text and to agree with the statements. This sentence is hard to understand. In addition I do not see that in group 2 in summer and in group 1 in autumn the OOA fractions are significantly larger than in the other groups of the respective measurement periods – they all seem quite similar. In addition: What do the authors mean with “longest trajectory”? Indeed, for the simulated time interval (48 h) the group 2 and group 1 trajectories are the longest ones. This means that during the last 48 h before arrival the aerosol has traveled the longest distance for these groups. However, for OOA generation it is probably rather a question of how large the emissions of precursors are along the track of the air masses during the last couple of days than the velocity of the transport. For example group 2 trajectories from the summer field campaign arrived from the sea with probably little OOA precursor emissions. Thus it would be reasonable to assume lower OOA concentrations for this group compared to the other groups where the air spent several days over the continent before the measurement.

P9129L20: I also do not see larger SO4 fractions for the groups that are associated with air masses from the northwest and northeast.

P9131L4: Jiangsu province was not mentioned before. Please introduce first in the main text.

Figure 2: It would be easier to identify times of the day if the scale would be 0/6/12/18/24 instead of 0/10/20. (Also Figure 7b,d)

Figure 3: The summer and autumn mass spectra are hard if not impossible to distinguish. I suggest shifting one of the spectra by 0.5 amu.

Figure 10: Are the fits forced through zero? Can you give the fit equation in a more meaningful form, e.g. PMF BBOA = 1.06 x estimated BBOA?

Figure 11: It is impossible to distinguish the two types of symbols in the graphs.

Figure 12a: What are the blue dots? What are the green and red symbols?

Interactive comment on Atmos. Chem. Phys. Discuss., 14, 9109, 2014.

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper