Atmos. Chem. Phys. Discuss., 6, S6567–S6574, 2007
www.atmos-chem-phys-discuss.net/6/S6567/2007/

Atmospheric
Chemistry
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Discussions

Interactive comment on "Source apportionment of submicron organic aerosols at an urban site by linear unmixing of aerosol mass spectra" *by* V. A. Lanz et al.

V. A. Lanz et al.

Received and published: 26 January 2007

The authors would like to thank H. Coe for reviewing our manuscript and for proposing helpful improvements.

We first like to make a more general remark since there might be a misunderstanding about the approach used in our study for identification of sources and aerosol components: The measured reference spectra from literature (or derived from the data - see item 1 below) were used to validate our results (estimated source profiles), they were not used to model neither source profiles nor contributions. Even though this validation is very important, one should keep in mind that the choice of reference spectra and the way they were calculated does not alter the PMF results in any way. The PMF results

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(i.e. the estimated source profiles in Fig. 3 and the time series of their activities in Fig. 6) are derived from a bilinear factorization of the measured data matrix - in other words: both the source profiles (F) and the source strength (G) have to be estimated (p. 11688/11689, lines 25-26/1-5) without any a priori information (with the exception of general non-negativity constraints). This is different from a CMB-like approach, where reference spectra are used to estimate source contributions - this is not the case for PMF based analyses.

In the revised manuscript, we will describe the concept of the applied approach in more detail in section 3.2.1., where the reference spectra are introduced and in the section about PMF theory (3.1.).

1) The charbroiling reference spectrum was derived from our data set as no such spectrum could be found in the literature. This reference spectrum was derived based on observations of charbroiling taking place in the immediate vicinity of the measurement site. Charbroiling events were observed repeatedly at this site and should not be excluded from the data set as it is obviously representative for the urban summer situation there (and probably at many others sites as well). We are fully aware of the fact that there are urban background sites that are less influenced by such activities and therefore carefully stated that Zurich-Kaserne is likely to be more biased towards charbroiling (p. 11707, line 13).

Those observed charbroiling plumes (lasting several minutes) typically gave rise to higher concentrations than typically measured at that site and given the time of observation, events of charbroiling aerosol emissions could be identified and analyzed in a straightforward manner: the absolute signals of three events (typically lasting 14 to 28 minutes each) were averaged separately and the absolute signals of about one hour sampling time before those events were averaged as well and subtracted from each isolated charbroiling peak. Then, those three spectra were normalized and averaged again (to give equal weight to each of those events). The data set was further tested for similar spectral signatures as the ones that were identified based on observations:

other peaks (not observed) of similar spectral signature (i.e. charbroiling-like) nicely meet expectations (in terms of hour of the day and weather conditions) when charbroiling should have taken place. More charbroiling spectra have been calculated based on those latter peaks and different approaches to subtract the aerosol background have been applied (e.g. averaging all signals between two identified charbroiling events, i.e. typically 20h-means if there were such events on consecutive days): the spectral fingerprint of charbroiling was found to be similar for those additional peaks and independent of the background subtraction technique used. Barbecue activities however possibly emit a vast range of different particles (depending on the type of charcoal, different types of vegetables or meat that is grilled, use of accelerants, phases of glowing, quenching,...): it will be the subject of future investigations to show which processes are most contributing to the specific fingerprint found here.

There are no spectral indications that the charbroiling spectra derived from the data set may contain wood burning contaminations. The relative intensities of both wood burning tracers m/z 60 and m/z 73 are below 0.5% in the charbroiling reference spectrum that was derived as described above and normalized according to Equation 5. On the other hand, measured wood burning spectra (Schneider et al., 2006) exhibit normalized intensities of m/z 60 and m/z 73 that are between 0.7%-7.5% and 1.6%-5.7%, respectively (calculated from beech, oak, spruce, and levoglucosan mass spectra). Those intensities are even higher for secondary organic aerosols (SOA) due to cyclopentene (CP) oxidation (Bahreini et al., 2004) than for the charbroiling MS derived from the present data set: the m/z 60 signal is at 0.8% and m/z 73 is at 1.1% there. Both comparisons are indicating that our reference spectrum is free of wood burning contamination. (The example of SOA due to CP oxidation also shows that low intensities in m/z 60 and m/z 73 should not be over-interpreted). In any case, the calculated time series (e.g. of wood burning or charbroiling) are independent of the choice and calculations of those reference spectra (see general remark above).

There is no doubt that the time series (PMF retrieved) that can be interpreted as wood burning and charbroiling are correlated with each other. In summertime, both wood burning and charbroiling are most probably due to leisure activities. Therefore, both sources are more likely to be active in the evening, on weekends, on holidays and during nice weather (clear sky, high temperatures). It is therefore not surprising that those time series are correlated to some extent. This issue has been raised by referee #1 as well ("Detailed comments") and will be addressed in the "Discussion" part when revising the manuscript.

2) The separation of oxygenated organic aerosol (OOA) into two distinct types of OOA (OOA, type I and OOA, type II) is not dependent on any particular reference spectra (see general remark above). The concentration of OOA, type I is correlated with particle-sulphate concentrations measured by the AMS and exhibits spectral similarity to several reference spectra of aged particles. We have observed that OOA, type I is very similar to aged particles that were measured (it is not the result of an 'Algorithm 2' based component analysis) at a rural site (Alfarra, 2004). On the other hand, the OOA reference spectrum taken from Zhang et al. (2005a) was not extracted from a remote/rural site. It has been extracted from an urban data set and we therefore have some confidence in it. The performance of the Zhang et al. (2005a) approach for rural data sets is, however, of no concern here. OOA, type I, also exhibits spectral similarity to highly aged particles at urban sites (as well as to the MS of fulvic acid and to some extent to the MS of humic acid).

It should be noted that we do not argue that any component (including OOA, type II) might be due to isoprene oxidation. We only state that the aerosol component OOA, type II can chemically be best represented by/ is most similar to the MS of SOA that is formed by oxidation of isoprene. It is discussed in the manuscript (section 4.4.1.) why OOA, type II is probably due to "accumulation of oxidation products formed during the day that condense onto pre-existing particles at night" (p. 11699, lines 21-22).

3) In the revised manuscript we will put more emphasis on PMF diagnostics. Please consider our replies to referee #1 (item 3) and to P. Paatero. We believe that multi-

variate statistical approaches like PMF are powerful for retrieving source information from AMS data and we demonstrate the usefulness of such an approach in the present manuscript. However, we would not consider our manuscript a “blueprint” for future similar analyses of AMS data. There is no guarantee that a bilinear model as used in our study can be successfully applied to any characterization of ambient aerosols using an AMS. In fact, we have learned from AMS measurements during winter when the variability of the data was driven by meteorology rather than by source strengths that a different model (a bilinear model that includes a priori source profiles) was needed to separate the impact of the main sources and aerosol components (Lanz et al., in preparation).

4) We fully agree with the referees H. Coe and P. Paatero that the sixth factor should not be over-interpreted. Consequently, we labelled the sixth factor carefully as a minor source that is influenced by food cooking (see below). As it seems that our interpretation of the sixth factor is easily read over, we will therefore state this interpretation more carefully throughout the revised manuscript (as specified below).

Minor Corrections

Page 11684, Lines 5-10: As suggested by referee #3, the reference Zhang et al. (2005a) will be deleted from the first paragraph on established approaches for SOA estimation because it “is an overstatement that the Zhang-Jimenez study is careful not to make”. In the revised version, the approach by Zhang et al. (2005a) will be addressed and discussed separately in the second paragraph. As suggested by referee #1 and P. Paatero, the issues of two sentences (on lines 8-13 and 16-19, respectively) will be reworded as well.

Page 11684, Line 13: “acids” will be changed to the singular “acid” in the revised version.

Page 11685, Line 22: The referee’s suggestion will be implemented in the revised manuscript.

Page 11687, Lines 3-8: We agree with the referee that the results reported in our manuscript and their interpretation is not dependent on the applied CE value. We also agree with the referee that a comparison with a PM10 measurement is not the ideal way to determine the CE. We, therefore, will rephrase the paragraph referring to the CE determination as already mentioned in our reply to referee # 1, item 2.

Page 11688, Lines 16-17: The word “samples” directly before the comma will be deleted.

Page 11690, Lines 17-18: We fully agree that fulvic acid can best be described as “a model compound that describes the chemical functionality of aged, oxygenated aerosol”. This will be made clear in the revised manuscript.

Page 11693, Line 6: It is correct that “its” should read “their” here.

Page 11694, Line 4: Zhang et al. (2005a) will be cited again here in the revised manuscript. This will certainly give helpful additional guidance for the reader.

Page 11695, Line 12: “loosing” will be replaced by “losing”.

Page 11696, Lines 1-4: As we do not equal the sixth factor to food cooking on p. 11703 but rather label it “Minor source (influenced by food cooking)” we will - for reasons of consistency - also reword the corresponding lines above (e.g. p. 11696, lines 1-4). This comprises to stress that our finding is an indication for a fragmentation that resembles an oleic acid type signature that may arise from food cooking. In addition, the lack of a measured reference spectra for food cooking (rather than model substances for food cooking such as oleic acid) in the AMS literature will be addressed.

Page 11697, Lines 22-23: The referee raises an interesting comment about particle ageing. We are also very interested to know how stable certain compounds in the aerosol are. However, this data set is not suited to answer this question. Our study is based on receptor-only measurements: an “average” wood burning MS is calculated for all wood burning sources. At an urban background site, polluted air masses from different sources and also masses of different age are superposed. The best way to study particle ageing would probably be a Lagrangian setup where air masses of different age could be probed.

Page 11698, Lines 20-21: “nice” will be replaced by “anticyclonic, stable”.

Page 11699, Line 6: We would expect fireworks in the evening of August 1 rather than in the morning. We do not expect that private activities in that field are likely to cause the error structure observed during all morning. It is probably caused by the fact that relatively low mass concentrations prevailed on that morning (see below and Fig. 1). We however cannot completely rule out that such things contributed to some minor extent.

Page 11699, Line 4 and Figure 5: Periods outside photochemical activity usually can be described by less aerosol mass concentrations, implying less absolute errors. If on the other hand Q (or squared scaled residuals) per row (or sample in time) are inspected, the differences between photochemical and non-photochemical phases are not prominent - despite the expectance that source-receptor profiles are not constant: this is an indication that reactivity during photochemical periods can adequately be described within the present model by means of both aerosol components OOA, type II as well as OOA, type I. In the revised manuscript, this will be shown by introducing a plot Q versus sample in time.

Page 11699, Lines 17-18: We agree with the reviewer that the mass spectral signature of fulvic acid was not similar to that of SOA produced in the smog chamber under high initial precursor concentrations. The relation of OOA, type I and OOA, type II in comparison to secondary organic aerosol measured in smog chambers at different concentrations is very interesting and currently under investigation. This surely is a topic by itself that will need further work.

Page 11702, Lines 15-16: The referee is correct: the argument should be put the other way around in the discussion of wood burning plumes on 1 and 2 August 2005.

Page 11703: We agree with the referee that indications provided in this discussion are too ambiguous to conclude that the sixth factor can fully represent food cooking. Therefore, we never claimed that the sixth factor should be interpreted as a pure food cooking source. We stated with care that “the sixth factor can be interpreted as influenced by cooking” (e.g. p. 11703, line 10) and labelled it “Minor source (influenced by food cooking)” (p. 11703, title of section 4.4.3.). We will carefully check whether we have missed a passage where it is claimed that the sixth factor would equal food cooking and will restate this point even more carefully.

Page 11723, Figure 7: It should read “bottom/left” instead of “bottom/right” in the caption of Fig. 7 - but please note that we probably will omit the notches in Figures 7 and 9 as this information may not be too important there (see our reply to P. Paatero, item 7).

Interactive comment on Atmos. Chem. Phys. Discuss., 6, 11681, 2006.