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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Cluster analysis of the organic peaks in bulk mass spectra obtainedduring the 2002 New England Air Quality Study with an Aerodyne aerosol massspectrometer" *by* C. Marcolli et al.

Anonymous Referee #2

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General comments

The paper "Cluster analysis of the organic peaks in bulk mass spectra obtained during the 2002 New England Air Quality Study with an Aerodyne aerosol mass spectrometer" by C. Marcolli et al. is an interesting paper that presents a new method for the analysis of the organics mass spectra measured with the widely used Aerodyne Aerosol Mass Spectrometer AMS. This topic is well suited for ACP since the general understanding of organic aerosol is still too low but is needed for detailed modelling of aerosol chemistry.

While this is an interesting and important paper that deserves to be published, I have some general critical remarks on the method, and I would like to see the authors discussing their method, their findings, and the benefits of their method more critically before publishing in ACP.

The authors use a hierarchical cluster algorithm that was developed for clustering mass spectra from single particles, measured with a laser ablation time-of-flight mass spectrometer (PALMS). The algorithm is based on the fact that one has full mass spectrometric information for every single particle that is included in the analysis. This given, it can be compared if different particles look similar in terms of composition or not. The quadrupole AMS used in this study is an aerosol ensemble instrument, which can not analyse the particles one by one (because a quadrupole is scanning ion filter), but needs to average over a certain number of particles in order to obtain a representative chemical composition of the averaged particle ensemble. Thus, I would conclude that comparison of mass spectra can only be done if the spectra have been averaged over the same number of particle or, even better, over the same organic aerosol mass concentration. The authors mention this issue on page 4611, line 20-23, when they find that the diversity is higher when organic mass concentration is low. However, their discussion remains vague: Knowing the absolute particle concentration (very likely a CPC was on board, maybe even an SMPS?), the authors can calculate how many particles were averaged. This result can be related to the measured organic mass concentration and the size distribution, and by that it can be estimated if the averaged aerosol ensemble is representative or not.

In general, I would recommend using an averaging algorithm that averages over an aerosol-mass-weighted time period instead of over a constant time period of 2 minutes.

Secondly, if one samples with the AMS within one "air mass" (the definition of which is not always clear in atmospheric science), then it is not surprising that the mass spectra, if averaged over a representative amount of particles, look similar. Thus, clustering averaged aerosol composition data within one air mass doesn't make sense to me.

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I would like to see if the result is the same if one independently classifies the air masses by other tracers, (e.g., O3 levels, isoprene levels, or backtrajectories), and subsequently averages the mass spectra from each air mass and compares this result with the dominating clusters. From the result given in Figure 11 (comparison with isoprene and ozone), one would expect to find similar "clusters" or "averaged MS over one air mass".

At the end of section 3.2 the authors make use of the delta analysis (pages 4610/4611 and Figure 6): Does the finding that there are no pronounced differences in the delta patterns imply that categories 1 through 5 are so similar in the MS signatures? Or does is imply that the delta-analysis is not sensitive enough? Is it really important to show Figure 6 or can the finding be described in the text?

Figure 5: Why do the authors use in the cluster algorithm the scalar product to compare mass spectra and now the correlation coefficient? What is the advantage of either of these methods and why is each of them used? Would they yield the same result? What are the advantages of using r^2 instead of r?

Specific comments:

Page 4606, lines 3 to 15:

The dot product (maybe better called "scalar product") of two identical vectors is unity if the vectors are normalized to unit length. When a mass spectrum is normalized to unit intensity, every peak intensity is divided by the total intensity (the sum of the individual intensities). In order to normalize the mass spectrum like a vector to its absolute value (the length of a vector), the peak intensities have to be divided by the square root of the sum of the squares of the individual peak intensities. Only in the latter normalization, the dot product of two identical MS yields unity.

Page 4606, line 13: The scalar product ("dot product") should be written as $A \cdot B$, and not as $A \times B$, since the latter is the vector product.

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Page 4607, line 2, and p. 4608, line 24: Was the nitrate signal at m/z 30 subtracted? Isn't it possible to infer the NO^+-signal on m/z 30 due to NH4NO3 from the ratio 46:30?

Frequently the term "Pittsburgh Aerosol" is used. I would recommend using "oxidized urban aerosol" since most likely this type of aerosol is not specific for Pittsburgh, e.g.: Page 4610, line 16 Replace "the Pittsburgh oxidized organic aerosol" with "the organics aerosol measured in Pittsburgh in (season, year) by Zhang et al.".

Page 4612. line 9: Replace "Pittburgh OOA" with "the oxygenated organic aerosol measured in Pittsburgh by Zhang et al.".

Figure 4: Replace "Pittsburgh OOA" by "oxidized urban aerosol"

Page 4611, line 18-20: "The low diversity...". This sentence is pure speculation and is disproved by the following statement. I would suggest skipping it.

Technical corrections:

p. 4616, line 17: replace "Klinedienst" by "Klinedinst"

Interactive comment on Atmos. Chem. Phys. Discuss., 6, 4601, 2006.