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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 #3

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General Comments

This paper applies a hierarchical clustering algorithm (HCA) to data collected using an Aerodyne Aerosol Mass Spectrometer (AMS) off the coast of New England during the summer of 2002. This is the first time such an approach has been taken using AMS data, and the subject matter is certainly appropriate for ACP. However, there are some problems associated with the methods, and in general, I do not believe that sufficient evidence is presented to support the conclusions made. The paper is mostly well written, with an appropriate abstract.

Specific Comments

In the abstract, the wording of ‘as much as 5 ug/m3 organic aerosol mass - 17% of the total organic mass’ makes it sound as if the total organic aerosol mass was always approximately 30 ug/m3, which is clearly incorrect (line 17 in the abstract).

The paper should, without a doubt, provide support to the use of a single-particle data analysis technique for an instrument that yields data that represents ensemble averages of particles in the atmosphere. By using an ensemble instrument, different types of particles may be masked by one another through averaging - and then again by clustering.

There is a problem with equation (2) and its discussion. The dot product is one only if the vectors are normalized. In addition, equation (2) shows the cross product, not the dot product of the vectors.

Section 3.1 (lines 20+ on page 4608). More detail is needed on how nitrate peaks are handled. I do not believe it is appropriate to include all of the peak from m/z 30 as part of an organic study. Some of this no doubt comes from inorganic nitrate - even if it is not ammonium nitrate (though my gut tells me even a tiny bit of that will form even in sulfate rich/ammonia poor conditions). The study is conducted in the polluted marine boundary layer where high concentrations of nitric acid will react with sea salt particles in the size domain in which the AMS can collect particles, yielding sodium nitrate. Is this nitrate potentially due to sodium nitrate? Nitric acid may also sorb to particles - yielding ‘pure’ nitric acid in the aerosol phase. Could this not also be a source of signal at m/z 30? The authors, at least in this manuscript (one other in preparation is cited) have not provided enough evidence to support inclusion of the peak at m/z 30 as ‘organic.’

On page 4610, lines 4 and 5 - why are these m/z ratios chosen? What do these values represent?

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Interactive Comment

In the following paragraph, it is not clear to me why removing the peak at m/z 44 is necessary, especially since it is a dominant contributor to signal.

Also in this paragraph, no where is it specified what type of oxidation system was used in the alpha-pinene study of Alfarra et al. Is the use of a different oxidant the reason for the differences in the spectra shown for that study and that of Bahreini et al.?

Page 4611, line 1+ - the authors state that the average delta patterns for the top 5 categories are similar to each other and more similar to those from biogenic precursors than those from anthropogenic precursors. Two comments: One, for non mass-spec specialists, a little bit more detail on what a delta pattern represents would be helpful. Two, I suggest changing the word anthropogenic to aromatic - to my knowledge, the delta patterns of SOA from anthropogenic species other than aromatics are not known.

In general, I find the discussion of relatively minor categories not particularly meaningful, especially since they were observed during low mass periods when relatively fewer particles were being sampled. I would suggest focusing more on the most important categories.

Page 4614, first paragraph of section 3.4. Why is the peak for category 1 much broader than the organic aerosol distribution with the peak in the afternoon if both represent SOA of a given type? Why does the category 1 distribution also feature a peak at night?

Page 4615, the authors discuss correlation with gas phase species of some of their clustered categories. However, they use rather vague descriptive words (i.e., well, to a lesser degree). Please provide the numbers as it is difficult to really look at correlations on a time series plot on which multiple variables are plotted (Figure 11).

A key issue with the paper is stated on this page (lines 14-15): 'implying that during this time period also the particulate organic mass represented by category 1 could have biogenic sources.' Elsewhere, they discuss the conversion of categories other

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than 1 to category 1. Therefore, the authors can not say what fraction of their SOA is biogenic vs. anthropogenic. In addition, the converse may be true - that there may be some unidentified anthropogenic that contributes to categories 2-5 (especially given the ensemble type of measurement). Therefore, it is unknown what the bounds on their estimate are. In addition, comparing to deGouw et al. certainly gives credence to their ideas. However, it must be even more strongly underscored that the method of deGouw completely ignores monoterpenes as an SOA source. In section 3.6, method 1 is not appropriate.

Section 3.8 should be removed.

Comments on Figures:

Why are two different plates required for Figure 1?

Figure 2 (and elsewhere) - high-resolution wind direction measurements may not necessarily represent air mass history. I suggest use of some back trajectories.

The text in Figures 5 and 7 is small and difficult to read.

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