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Comment

Interactive comment on “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.

Anonymous Referee #1

Received and published: 27 July 2006

The paper presents the first use of a data analysis tool based on hierarchical clustering, first developed for use with the PALMS laser ablation single particle mass spectrometer, to deliver information on the mass spectral fingerprint of organic material as measured by the Aerodyne Aerosol Mass Spectrometer. In my opinion this is a very worthwhile goal as there is a considerable amount of information in the organic mass spectra of the AMS that has to my knowledge not yet been mined effectively. The paper also tries to identify on the basis of these clusters the sources and processing of the measured organic aerosol mass. It goes some way to convincing the reader that several of the

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categories are likely to be biogenic nature, but this is largely by comparison with gas phase precursor data that from the derived MS. It also tried to convince the reader in several places that the biogenic signatures seen in several classes age towards the primary oxygenated class. There is no sound basis for this argument and the authors need to speculate once and leave it there.

The paper is well written and offers some new insights and makes a valuable contribution to the body of work associated with the development of the AMS. Several referees have already commented extensively on this paper in considerable detail. In particular, referee 4 makes a number of very important detailed points that need to be considered. The authors' responses to these points are largely well considered and I will not dwell on those in this contribution. There are, however, one or two points that remain outstanding that I feel should be considered by the authors.

The main problem area in the paper, which is identified by all the reviewers, surrounds the validity using a method developed for clustering different particle types together based on a measurement of the chemical characteristics of single particles and probing the number frequencies with which these clusters are observed, and applying it to an data stream that delivers data on the composition of the ensemble of particle in the atmosphere in a given time interval.

There is nothing incorrect in such an approach in itself and it can, as the authors show deliver significant insight into the organic mass fraction of the aerosol. However, what is missing from the paper is a real discussion of what information can be retrieved from such a method and what the pitfalls are. Hierarchical Cluster Analysis essentially groups similar mass spectra together over a given time interval to form a small number of clusters that are of distinct character. However, when applied to PALMS and AMS data this means two very different things. In the case of PALMS, the individual mass spectra represent chemical signatures of different particles and the clustering represents a way of grouping chemically similar particles together and assessing the relative frequencies of occurrence of these groupings i.e. how many particles of a given

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type are sampled in a given period.

When applied to AMS data the analysis means something quite different. This message is not really stated explicitly and in my opinion it should be. The criticisms made by the reviewers are fair and could be addressed with a separate section in the paper entitled something similar to “Differences between using Hierarchical Cluster Analysis for analysis of single particle and ensemble averaged mass spectrometric data”. This should lay out the general applicability of the method for single particle and ensemble averaged data sets and highlight what is delivered and what cannot be inferred from either method. The remainder of the paper should then be an assessment of the power of HCA on ensemble averaged data and its shortcomings, as it is currently written, with an extension of the discussion section as indicated by reviewer 4. I will not go into detail of what is being done as several of the reviewers have laid this out previously. I will though offer a simple example that illustrates the points made by referees 2 and 4.

Suppose a high mass loading is experienced for a small fraction of time in a given period and the rest of the time low loadings are observed. The current analysis will provide a fixed number of MS distributed evenly in time, each of which are normalised. So the period of high loading is neither proportionately represented on either a mass or number basis but on a temporal basis. When the MS are combined based on their similarity to obtain different classes, the information on mass or number population will not be immediately available. Rather, what is represented is a comparison of the relative dominance of a cluster type during a given time period. However, by combining the results with other forms of time series and correlation analysis the types of aerosol contributing to the AMS data record in certain periods can be identified and some conclusions drawn. This is what the paper is about and it can have an important contribution to unpicking different organic aerosol classes.

I have no doubt, given by the authors' responses to the previous reviewers, that they are aware of the benefits and limitations of the method. However, the authors do not convey the essence of these complexities in the current version. To save the reader

or subsequent user misconstruing what the paper is trying to achieve and to make it plain what is being tested I would like to see that at the end of section 2 Experimental Methods, the authors spend a paragraph or two discussing these issues in a separate sub-section 2-2. I am sure this will leave the reader in no doubt what can and cannot be done and how the results should be interpreted. The following sections then serve as a test of the power of the method.

The second area I wish to discuss is the use of the method on this type of dataset. As far as I can see the clustering works by finding the minimum dot product of two MS from evaluating every pair of MS in the whole dataset, averaging these two MS and then repeating the process on the reduced number of MS until a certain number of MS groups remain. At each stage the clustered MS are treated identically to a signal MS and with the same weighting, at least I see no comment to the contrary. In effect this means that a final cluster is an average of two mass spectra, both of which may be groups of a large number of MS but they may be simply an average of a large group and a single MS. In the latter case the final MS will be significantly different from the bulk of the MS in that class or for that matter from either the mass averaged MS or the number averaged MS (the latter can be gained by normalised each MS in the class and averaging them). It may be useful to compare these and illustrate the differences. The use of HCA is very useful for identifying aerosol types and atmospheric conditions and is therefore a key weapon in the data analysts arsenal but great care needs to be taken when using the MS retrieved from this type of analysis as it can be greatly biased by the way the classes are formed. As in this paper the final classes derived from the field data are then compared with single MS taken from the laboratory, the authors do need to discuss this and take great care to convince the reader that such effect are small.

The last main area I wish to pick up on is the area of counting statistics and the use of zeroing the negative mass peaks in the individual MS prior to averaging. This is something picked up on by reviewer 4. The response by the authors is not satisfactory in my opinion, nor is it in the mind of reviewer 4. I will again illustrate the problem I have

with an example from the paper. Suppose that the particle population is chemically identical in two separate periods but the mass concentrations are different such that in the first period there is considerable mass and many peaks show signal well above the noise level. In the second period, the signal is much lower and many more peaks are not present above their detection limit. In the latter these peaks would be set to zero and the relative importance of the remaining peaks would dominate. Hence two distinct clusters would be present for two populations that are chemically identical. This will not happen when applied to the PALMS data where the ion yields from single particles can be directly used. The authors really need to consider this aspect it can seriously compromise the results if one is not very careful. I suspect that the clusters 7 and 13 suffer from this. The relevance of cluster 13 in these circumstances must be questioned. I would strongly urge the authors to apply some criteria to ensure that an artefact of this type does not occur. As reviewer 4 states, I fail to see the need anyway.

Specific Comments:

Page 4607 line 17 insert 'a'.

Page 4607 line 20-25 The dataset was divided into 4 parts and the analysis was run separately to start. This implies that after some period all the data were combined to complete the analysis. Was this the case, it should be said explicitly? Though this eases the computing requirement does this compromise the data analysis in any way?

Page 4608 line 8: “..quite small molecules or strongly” reword to “..quite small molecules or was strongly”

Pg 4608 line 25: m/z 30 can also be due to non nitrated organic, this needs to be said.

Pg 4611 line 2, but only a few spectra of simple anthropogenic systems are available and it is widely acknowledged that these may not be representative of anthropogenic SOA as a whole.

Pg 4612 line 1: “Although the contribution to any wind direction” surely you mean

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“Although the overall contribution across all wind directions.” as the first statement is not true for some particular directions.

Pg 4613 lines 8-11: The argument made here that the maximum organic mass being observed in the afternoon and correlating with the solar radiation is consistent with SOA formation and gas to particle partitioning only holds if the SOA formation is in situ. Is this likely to be the case? If true this implies a formation rate of around 0.6 $\mu\text{g m}^{-3}\text{hr}^{-1}$. This is pretty substantial and implies significant photochemistry. Category 1 dominates the aerosol mass and shows the same feature, yet the argument is made elsewhere that cat 1 is aged aerosol. It is therefore unlikely that such an appreciable amount of SOA will form in such well aged aerosol, essentially the organic aerosol mass changes by 10% per hour a significant production rate implying a youthful and very actively photochemical airmass. The authors need to discuss this in more detail.

Page 4613 lines 20-24 This is speculation as far as I can see there is no justification for arguing that processing is responsible for transforming cat 2 to cat 1. The arguments that lead to a source of cat 2 have some merit but cat 1 can arise from either anthropogenic or biogenic sources from the results presented. In fact cat 1 arises from air masses impacted by pollution by and large and not from other regions implying pollution plays a role, either as the source of the SOA or by creating the photochemical environment in which the SOA are formed to give the fragmentation pattern observed.

Pg 4614 lines 1-5 as stated by another reviewer I believe, the photochemical marker is only of use for anthropogenic air mass tracing and aging. It is meaningless for biogenics.

Pg 4614 section 3.5 I rather agree with reviewer 4. This discussion is rather speculative. Some back trajectories, estimates of time from source and possibly source modelling is required to investigate whether the timescales postulated are reasonable.

Pg 4615 bottom again this is pure speculation, there is nothing definitive here at all, statements such as this should be removed. The accumulation of statements like this

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leads to the reader's overview that it has indeed been shown that cats 2-5 are transformed into cat 1, it has not.

Page 4616 line 12: The products do not need to be the same, simply the chemical functionalities of anthropogenic and biogenic products, it is these that give a characteristic signature to the AMS.

Section 3.7 See my general point, to what extent are 7 and 13 different, can artefacts due to zeroing sub noise data be excluded?

Page 4619 I agree with referee 4, this section needs to really explore what the technique is telling us and what its shortcomings are.

Figure 1 Use degree symbols for latitude and longitude

Figure 9: top panel left axis label should read microgramme not gramme

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

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