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Atmospheric
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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 #4

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This paper covers the application of hierarchical cluster analysis (HCA) to the AMS dataset collected aboard the Ron Brown during the 2002 NEAQS study and the scientific outcomes of the analysis. This algorithm was developed for the PALMS instrument and in this case, instead of being applied to single particle mass spectra, is being used for the first time on averaged 2-minute non-refractory ensemble mass spectra produced by the AMS, in particular, the organic fraction. Particular attention is paid in the text to the biogenic fraction. These are very relevant subject areas for ACP, as there are many gaps in understanding in the lifecycles and impacts of organic aerosols and the AMS

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has proved to be a very useful tool in probing these in recent years. However, as the AMS produces very large datasets, the usefulness is very dependent on the reduction methods used, the development and application of which is the technical motivation for this work.

While there are some issues with the mathematical methodology (see below), the paper does show that HCA is a useful tool in identifying clusters of similar measurements within a dataset. These can be employed to facilitate the further analysis, either by comparing with other measurements and source identification or inspecting the representative spectra of each cluster and comparing with reference spectra. This technique may also be useful in probing the 'partly oxidised' mass spectra, frequently observed by the AMS when sampling regional emissions, that conform to neither the model 'hydrocarbon-like' or 'oxidised' organic aerosol defined by Zhang et al. (2005a).

Unfortunately, as described below in the specific comments, the paper runs into problems when trying to interpret the clustering output further. The single biggest problem is that the technique of generating time series of 'occurrences' opens many interpretive pitfalls. There is a temptation to treat the occurrence data as independent, linear representations of different chemical fractions encountered during the measurements in a similar manner to principal component analysis. While this would be true for single particle mass spectrometers sampling external mixtures, it is very far from the case for an ensemble instrument like the AMS, where combinations of many different components are reported in the mass spectra. The exact category that any given spectrum will be associated with is determined by a complex combination of different factors including the precise proportions of the chemical species present, the other spectra contributing to the various clusters and the amount of random variations within the signal. Obviously, a spectrum containing only one component with a high signal-to-noise will be clustered appropriately, but a spectrum containing a mixture of two or more will be ill-defined. In addition to these ambiguities, the derived occurrences will be highly sensitive to the overall amount of variability experienced within a particular 2-hour period and not necessarily a reflection of the actual chemical concentrations. For example, if the derived occurrence of a hypothetical category ’A’ decreases while an occurrence ’B’ increases, it does not necessarily mean that the actual chemical concentration of the component that ’A’ represents is decreasing. It could equally be that a relative increase in the concentration of the ’B’ component causes it to dominate the mass spectrum and forces all of the spectra to be classed as ’B’ within a period, even if the ’A’ chemical component is constant or even increasing itself. Conversely, if the mass spectra were to somehow repeatedly change between being an ideal ’A’ and an ideal ’B’ numerous times within a 2-hour period, it is conceptually possible for the clustering to give an accurate representation of the time spent in each state.

To sum up my opinion, while the occurrence may be a useful qualitative indicator for identifying time periods of interest, without accounting for the coupling and nonlinearities in its derivation, it is largely unsuitable for quantitative work. Some of these subtleties are touched on in certain parts of the text, but they are not made obvious to the reader and in some cases conclusions are reached without taking them into account. A suggested method of addressing these criticisms would be to generate a modelled AMS dataset based on linear combinations of various reference spectra and simulated noise, apply the HCA methods and see how robustly representative the derived occurrences are of the applied fractional contributions. Separate to this, the reader should also be given some idea of the variability within the clusters and the averaged data, which could be achieved using error bars (or similar) on the figures.

Additionally, there are issues regarding the assignment of sources and precursors because there are many points in the manuscript where statements regarding airmass histories are made without adequate supporting evidence being presented. A suggestion for improvement would be the inclusion of back trajectories in the analysis.

Specific comments:

Page 4602, line 22: Consider changing ’is a useful tool’ to ’can be a useful tool’. While the technique evidently works for the study presented, the 2002 NEAQS dataset is fairly unique in terms of the platform and location and as such, this paper does not necessarily demonstrate the technique as universally applicable (see comment to the conclusions section).

Page 4602, line 17: The statement of "17% of the total mass" is slightly misleading. While it may represent 17% of the total mass observed during the voyage, this cannot be taken as representative of the region because different areas were sampled unequally.

Page 4602, line 25: The opening lines of the introduction are far too brief. This should be expanded and references inserted so that it can be put into context for a reader unfamiliar with organic aerosol processes and the application of AMS data.

Page 4603, line 25: Even with the elemental discrimination, the high-resolution TOF-AMS is still not capable of resolving individual organic species.

Page 4604, line 3: The Zhang et al. (2005a) method does use all the peaks in the mass spectrum for principal component analysis. The use of the variations within a limited number of peaks is to provide the initial 'seed' mass spectra for the analysis.

Page 4606, line 13: The dot product (raised point) symbol should be used here instead of the cross product (x) symbol on the left side of the equation. The vectors should also be identified as such with arrows above the letters (bold is conventionally used to denote matrices).

Page 4606, line 15: Technically, the dot product of two parallel vectors is the product of their scalar lengths. It is only unity in this case because they have been normalised.

Page 4607, line 2: The peaks at m/z 30 (NO+), 31 (15NO+), 38 (H37Cl+) and 41 (41K+) frequently have non-trivial inorganic ion signals from particulates (although the issue of nitrate is dealt with later in the text). Also, the ratios used to subtract the gas phase components from the relevant channels should be stated. If there is a specific reason why the Allan et al. (2004a) method was not used in this instance, this too should be stated, as this is the method most frequently used to extract organic spectra (for use in the Zhang et al. (2005a) analysis, amongst others).

Page 4607, line 4: I am at a bit of a loss to understand what the mathematical merit of subtracting the estimated standard errors is and what the resulting data chemically represents. Furthermore, I can also see potential danger in it; a large component of the calculated error for many AMS peaks is associated with the concentrations of residual gases within the instrument coupled with its overall sensitivity and these vary over time with significant changes associated with sampling large concentrations of organics, calibrations and instrument reconfigurations. The subtraction of the errors will therefore artificially add extra components to the time series that could potentially leave the dataset open to misinterpretations. The authors should possibly consider repeating the analysis without the subtraction, as the inherent inaccuracies will still be present with or without this operation.

Page 4607, line 4: The clipping at zero is also not given any justification. The negative numbers result as a combination of the background subtraction process and the uncertainties in the measurements. As such, they are not valid data points individually but the numerical filtering of negatives can place a positive bias on the overall mass spectrum thanks to the randomly-occurring positive artefacts. Therefore, the reasons why this has been performed in this case must be explained.

Page 4609, line 5: The authors should explain the "fragments differing by 14amu" more clearly.

Page 4609, line 13: The authors should state whether they believe the primary organic aerosol were completely absent or simply diluted to the point where they could not be easily distinguished from the secondary organics. The latter is probably more likely, but the text seems to be implying the former.

Page 4609, line 20: The source of the unpublished data should be stated.

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Page 4610, line 14: The work that shows the association between the peaks described and the carbonyl group needs to be cited and described.

Page 4611: The comparisons to chamber-produced spectra are very informative, but in themselves only provide circumstantial evidence to support the hypothesis that categories 2 to 5 are of biogenic origin. To date, only a limited number of anthropogenic precursors and oxidation pathways have been studied in controlled environments and no experiment has yet been able to recreate the fulvic acid-like response in the AMS typical of polluted environments. Therefore, it is equally possible that there may be other anthropogenic SOAs not yet produced in chambers that happen to resemble biogenic SOAs when sampled with an AMS. This possibility is mentioned briefly in the text but not adequately discounted. The statement of the categories being biogenic needs to be backed up with more supporting evidence; the comparison with biogenic tracer measurements in section 3.5 does part of this, but to strictly show they are entirely biogenic (which is the assumption made later on in the manuscript), they would need to be shown to exclusively occur in the absence of anthropogenic (and possibly pyrogenic) tracer species such as benzene (unless a removal process such as wet deposition had taken place in the interim).

Page 4611, line 18: As the AMS measures ensemble mass spectra, it is completely insensitive to repartitioning. Surely the most likely reason for the reduction in diversity is that when the mass concentrations are low, the signal to noise ratios of the peaks will also be low due to ion counting statistics (Allan et al., 2003a), which will increase the random variability of the data, thereby increasing the diversity?

Page 4612, line 9: Does "Pittsburgh OOA" mean the emissions came from Pittsburgh? The authors should be clearer here.

Page 4612, line 24: Further to the earlier point, what evidence do you have to discount the possibility that coincidences within random variations are responsible for the minor clusters seen at low mass concentrations?

Page 4613, line 9: A potential alternative reason for perceived diurnal relationships may be that a time series is more directly related to a 24-hour cycle in the wind fields or boundary layer structure rather than the incoming solar radiation, so this needs to be discounted. See also the related points regarding the coupling of occurrences that may explain the anticorrelations.

Page 4613, line 20: Analysis using a photochemical age metric that only applies to urban plumes strikes me as completely incompatible with the earlier assertion that categories 2 to 5 are purely biogenic in origin. One would think that the occurrences of the other categories decreasing with photochemical age is simply a symptom of category 1 becoming dominant in urban plumes of a particular age and in doing so, completely overwhelming any (potentially random) contributions from other categories. Furthermore, as the authors point out, arguments about chemical transformations during a plume's lifetime are only valid if a comparison were to be done with data from directly comparable airmasses, so the further discussion regarding factors 3-5 seems very shaky.

Page 4614, line 13: A plot showing back trajectories overlaying a land-use map would be very beneficial to the reader.

Page 4614, line 24: If the isoprene time series did something genuinely interesting, it should be shown in a figure rather than just described.

Page 4615, line 4: How can the statement that category 3 species are longer lived be made without explicit knowledge of the plume history? Could it not just be that the organics featured in other categories were simply dwarfing 3, so when their fractional contributions decreased, the occurrence of 3 increased? Also, why is the air sampled later in the plume necessarily chronologically further from the source? The statement needs to be qualified better (e.g. by using back trajectories) or removed.

Page 4615, line 10: Constant local wind directions do not always mean a constant source footprint and the change in the modelled isoprene source function would seem

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to indicate otherwise. Back trajectories and the incorporation of more gases (e.g. benzene and CO) into the analysis would make the argument much more rigid.

Page 4615, line 17: Quantities are needed when stating that the anthropogenic VOC concentrations were "relatively low". The presence of isopropyl nitrate appears to contradict this.

Page 4616, line 21: As discussed above, the assumption that all the mass observed during the periods identified with categories 2-5 is biogenic in origin is not completely justified in my opinion. Unless the further supporting evidence needed can be presented, the strength of this assumption should be toned down and additional caveats added to the conclusions.

Page 4616, line 23: Method 1 seems strange to me. As method 2 averages and weights the discrete mass concentrations as they are saved (albeit in an algebraically roundabout way), it would consistently yield far more meaningful results than taking fractions of the averaged (and therefore mathematically degenerate) hourly data, so why even bother with method 1 at all? The fact that they yield similar results only tells you about the lack of correlation between the changing category assignments and variations in the total organic mass concentration within individual hourly periods, nothing more.

Page 4617, line 16: Following the earlier point, the statement that the estimate is a lower limit is only as valid as the assumption that categories 2-5 have zero anthropogenic contributions for the entire dataset and it should be stated as such.

Page 4617, line 9: The statement that the agreement is "quite good" needs to be backed up with more than what can be seen on figure 12. A scatter plot and r2 statistic would be useful.

Page 4617, line 23: These arguments are difficult to follow, partly because the possibility that at least some inorganic nitrate was present in the data is not universally discounted (see below). Also, the lack of categories 7 or 13 during particular periods does not imply the absence of nitrates as they could be simply being dwarfed by the category 1 components. A repeat analysis using the time series of the m/z 30 signal intensity should be included, as this will represent the amounts of nitrates and amines present far more quantitatively than the category 7 or 13 occurrences.

Page 4618, line 20: The 30/46 ratio alone cannot eliminate the possibility that inorganic nitrate was present, as a mixture of organic and inorganic nitrate species could be coexisting. Another possibility is that some of the nitrate could be in the form of sodium nitrate on aged sea salt particles. This has been observed in other marine environments with an AMS and has shown to give a very high 30/46 ratio. As ammonium and nitrate are semivolatile and will only coexist in equilibrium on pH neutral particles, a straightforward test for the presence of internally mixed inorganic nitrate can be performed by inspecting the molar ratios of ammonium and sulphate.

Page 4619: In the interests of objective discussion, the weaknesses of HCA should be covered in this section. The reason it works on a mobile platform such as this is that the selective study of specific source regions and plumes was possible, which is not always the case, in particular during urban studies where complex mixtures are continuously sampled. Another intrinsic limitation of this technique is that beyond the initial inspection, it was unable to retrieve any further information regarding the behaviour within category 1. As this accounted for 75 % of the time the AMS was sampling, this is a major limitation. Might a possible area for future development of the algorithm be to apply weighting to the peaks, so a category is not dominated by one peak?

Page 4620, line 9: As stated in the previous comments, the conclusions reached regarding the specific precursors for the different categories should really only be treated as speculation at this stage. A complete proof will require closure with SOA formation theory and given that no-one has yet produced a model that agrees with atmospheric measurements, we are not at the stage where we can say this.

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Page 4620, line 17: The scientific context and applicability of the conclusions need to be stated. The current text is very technical in nature and does not properly cover the original objectives of the article.

Page 4631: To give the reader an indication of the amount of variability within each category, the authors should consider inserting error bars showing the standard deviations associated with the major peaks.

Pages 4636-8 and 4641: Similarly, figures 8, 9, 10 and 13 would be improved greatly if they indicated the variability within the respective bins, through either error bars or boxes and whiskers.

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