Atmos. Chem. Phys. Discuss., 6, S1928–S1942, 2006
www.atmos-chem-phys-discuss.net/6/S1928/2006/

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.

C. Marcolli et al.

Received and published: 20 July 2006

We thank the referee for his/her detailed and thoughtful comments, which we have addressed in detail below.

Response to general comments: We agree with the reviewer that we did not discuss the particularities and pitfalls of the hierarachical cluster analysis in great detail. We improved this in the revised manuscript (see responses to specific comments).

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).

Response: We think that hierarchical cluster analysis is in general a useful technique to gain an overview over a large dataset. It should not replace other analysis methods as e.g. the one described by Zhang et al. (2005a) but complement it.

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.

Response: We change the sentence to: Taken together, the second through the fifth most common categories represent on average 17% of the total organic mass that stems likely from biogenic sources during the ship's cruise.

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.

Response: We followed the reviewer's suggestion and have expanded the opening lines.

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

Response: We agree with the reviewer that high-resolution TOF-AMS is still not capable of resolving individual organic species, but it is able to discriminate between fragments with the same nominal m/z, which might indeed help to discriminate between aerosols from different sources.

Page 4604, line 3: The Zhang et al. (2005a) method does use all the peaks in the

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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.

Response: With this sentence, we did not want to imply that only three masses were used. We improved the sentence to: One method that has been used involves multivariate linear regressions, separating the ambient mass spectra into linear combinations of two (or three) components using m/z 44 and 57 (plus 43) as initial seeds for the deconvolution of the spectra (Zhang et al., 2005a).

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).

Response: We changed the symbol for the dot product from a cross to a raised point. In the nomenclature of the EGU journals, vectors are identified by Bold Italics, matrices by Bold Roman.

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.

Response: We have normalized the spectra to unity length and refer to this case. We have made this clearer in the revised manuscript.

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).

Response: We used the Allan et al. (2004a) method to remove contributions from air

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and inorganic ions and the signals at m/z 38 and 41 were not excluded. In the revised manuscript, we state this now more explicitly. We kept the nitrate masses because they can also originate from organo-nitrates.

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 artifacts. Therefore, the reasons why this has been performed in this case must be explained.

Response: We subtracted the average noise levels from the peak signals to give the channels with high noise level and low signal less weight. This procedure seemed beneficial when using the log of the signal for the cluster analysis. It was not important when the linear peak intensities were used. In the paper, we only show results for the cluster analysis with the linear peak intensities since the larger m/z were still too noisy and did not provide clusters with distinct patterns. We added to the manuscript the reason why we subtracted the average noise level and clipped the negatives at zero.

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

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clearly.

Response: We improve the sentence to: In many of the categories, m/z 57 is typically not a major peak. A strong peak at m/z 57 along with m/z 55 and other hydrocarbon fragments differing from these two masses in steps of 14 amu due to CH2 groups have been found in the AMS spectra from direct emissions of diesel exhaust (Canagaratna et al., 2004) and this distinct pattern has been observed in urban mass spectra during the morning (Alfarra et al., 2004; Allan et al., 2003b; Zhang et al., 2005a, b).

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.

Response: We add to the manuscript the following sentence: The hydrocarbon-like fraction described by Zhang et al. (2005a) might have been too dilute or highly processed to yield a specific signal in the mass spectra. Category 15 with 15 spectra was the only one with a strong m/z 57.

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

Response: The unpublished data was from chamber experiments done by one of the co-authors (Bahreini). We might be able to include spectra from more recent published experiments (Kroll et al., 2006) in the revised manuscript.

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

Response: Citations have been added to the text.

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

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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).

Response: For the present analysis, we tried to use all available information from the NEAQS 2002 dataset itself and from other AMS studies. In section 3.6 we assume indeed that categories 2-5 are entirely biogenic. We agree with the reviewer that this introduces a bias in the direction of too high biogenic. We think that this bias is overcompensated by the assumption that all of category 1 is anthropogenic. In the revised manuscript we state the caveats to the analysis in section 3.6 more completely by adding: On the other hand, a part of the mass especially in category 2 but also in categories 3-5 might be anthropogenic. The assumption that the mass in categories 2-5 is totally biogenic might therefore lead to an overestimate of the organic mass at times when these categories are abundant.

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?

Response: Repartitioning will also occur on timescales longer than 1 minute between air masses that mix. We mention the importance of counting statistics on page 4611,

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lines 20-23. When the organic mass was less than 2 microgram/m3, the mass spectra were obtained from roughly 100 particles. Therefore, we think that counting statistics partly but not totally explain the high diversity at times when the mass concentrations are low.

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

Response: No, it means that we base our analysis on the correlation of category 2 with the mass spectrum of Pittsburgh OOA shown in Figure 5. To make this point clearer, we change the sentence to: This further supports the notion of category 2 as being indicative of isoprene oxidation products mixed together with oxidized urban aerosol as established from the correlations in Figure 5b.

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?

Response: We think that the very small clusters containing only few spectra can be explained by counting statistics. The larger the clusters are the less likely this explanation becomes. We do not have any strict criterion to discriminate between meaningful and meaningless categories. We consider the preferential occurrence of clusters at certain time periods as a sign for a category that is specific for certain air masses. We therefore think that e.g. category 14 consisting of only 24 spectra is not an artifact due to counting statistics.

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.

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Response: The wind directions during the whole measurement period as shown in Figure 2 do not show any obvious diurnal cycle. We think that changing wind directions and sampling locations rather obscure than cause a diurnal cycle. We have also checked the influence of the solar radiation by looking at individual days rather than the average over the whole sampling period. The boundary layer structure can influence the absolute organic mass and perhaps the relative occurrence of categories. Because the diurnal profile in organic mass is similar to that of ozone (now included in Figure 9), increases in organic mass during the day are due to photochemistry rather than boundary layer mixing. Changes in the relative occurrence of categories due to mixing is likely to be noticeable in urban areas where the organic aerosol in the nocturnal boundary layer has a large component of hydrocarbon organic aerosol (HOA) from fresh anthropogenic emissions (Allan et al., 2003b; Alfarra et al., 2004; Zhang et al., 2005a,b). However, in this study the organic aerosol in the nocturnal boundary layer is composed primarily of oxidized organic aerosol. So variations in composition due to boundary layer mixing in the present case are not as dramatic. We therefore remain confident that the solar radiation is responsible for the observed diurnal variations of categories.

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 air masses, so the further discussion regarding factors 3-5 seems very shaky.

Response: We totally agree that the photochemical age determined by anthropogenic

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tracers only applies when the aerosol and the tracer have the same history. This seems to be the case for category 2 which is most abundant when the winds are from the southwest since this direction also hosts the source region of the urban plumes. We think that the low correlation of categories 3-5 just shows their independence of anthropogenic VOCs. We try to state our reasoning more clearly in the revised manuscript by writing: Since the photochemical age is determined from anthropogenic VOCs originating from source regions in the west or southwest, only a weak correspondence with the degree of oxidation for categories 3-5, which mainly occur during times with northerly winds, can be expected. The low correlation with photochemical age in Figure 10 is therefore consistent with the particulate organic matter in categories 3-5 being comprised of only minor contributions from anthropogenic precursors that have been oxidized during transport and aging.

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

Response: The same time period has also been analyzed in de Gouw et al. (2005) where also a panel (Figure 13a) with the ship track and wind directions is shown. We will directly refer to this panel in the revised manuscript. We also added a couple of sentences describing the flow conditions and refer the reader back to Figure 1. Specifically we now state: The occurrence of categories 1 through 5 is shown as a function of time in Figure 11 for July 25-26, the time period when winds were from the north and the ship was sailing off the coast of Maine (detailed ship track and wind directions for this time period are given in Figure 13a of de Gouw et al., 2005). At this time, the synoptic climate classification for the region was a Canadian high, characterized by northerly or northwesterly winds from over Canada (Keim et al., 2005) with relatively high monoterpene emissions, moderate isoprene emissions, and low anthropogenic emissions (see Figure 1). Biogenic organic aerosols were previously reported to be present during these conditions (Slater et al., 2002).

Keim et al., Climate Res., 28, 143-154, 2005

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Slater et al., Sci. Total Environ, 287, 221-239, 2002 (full references in the manuscript)

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

Response: The isoprene time series followed the monoterpene concentrations during this time period and is shown in Figure 5 of de Gouw et al. (2003). We will directly refer to this Figure in the revised manuscript.

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.

Response: We think that category 3 species are longer lived than category 4 and 5 species. This statement can be directly deduced from the occurrence of the categories since it refers to the relative not the absolute abundance. The air sampled later in the plume was longer exposed to sunlight since it was sampled later in the day. To emphasize this more we change the sentence to: Whereas the rise of category 3 is simultaneous with the rise of the monoterpenes, its decline is delayed, which might be indicative of category 3 consisting of more oxidized, longer-lived monoterpene oxidation products that become relatively more abundant than category 4 and 5 species with increasing exposure to sunlight.

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 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.

Response: Unfortunately, CO data are not available. In the revised manuscript, we will

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refer to Figure 13 of de Gouw et al. (2005) showing the ship track and wind directions and Figure 5 of de Gouw et al. (2003) showing that toluene decreased instead of increased with increasing category 1. There appears to be a slight change in the isoprene source footprint when the isoprene source function changes at 1500 UTC. We are more specific about the times being discussed in the revised manuscript.

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.

Response: We give quantities in the revised manuscript: toluene and iso-propyl nitrate concentrations were a factor five below plume values.

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.

Response: In section 3.6 we assume indeed that categories 2-5 are entirely biogenic. We agree with the reviewer that this introduces a bias in the direction of too high biogenic. We think that this bias is overcompensated by the assumption that all of category 1 is anthropogenic. In the revised manuscript we state the caveats to the analysis in section 3.6 more completely by adding: On the other hand, a part of the mass especially in category 2 but also in categories 3-5 might be anthropogenic. The assumption that the mass in categories 2-5 is totally biogenic might therefore lead to an overestimate of the biogenic organic mass at times when these categories are abundant.

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

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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.

Response: The text on method 1 was removed.

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.

Response: We have followed the reviewer on this point (see response to the comment referring to page 4616, line 21).

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.

Response: We agree that a scatter plot might be useful, however the sampling times are quite different - 5 minutes every half hour for the gas phase calculation and hourly averages for the AMS data. Furthermore, changes in relative occurrence are not always directly related to gas phase concentrations for many reasons. We qualify the agreement as quite good given all the assumptions and uncertainties connected with the biogenic mass derived from the categories. A scatter plot and r2 statistics would rather direct the attention away from the specific time periods when the agreement was good or bad and imply the possibility of a full agreement which can not be achieved given all the assumptions that had to be made.

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

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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.

Response: We did not intend to imply that the lack of categories 7 or 13 signifies the absence of nitrate. We have rewritten the discussion of the category results in section 3.7. See also the next response.

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.

Response: Inorganic nitrate was measured using ion chromatography for samples analyzed online with PILS (only submicron particles) and offline with impactors (both sub and supermicron particles) and the results of these measurements are reported in Quinn and Bates (2003), Brown et al. (2004), and Bates et al. (2005). Essentially very little inorganic nitrate was measured in submicron particles, with some nitrate detected in the supermicron particles in the form of sodium nitrate (impactor data). Comparisons of the AMS nitrate with PILS nitrate during times when submicron sodium and nitrate were detected with PILS, the AMS nitrate was low. Hence, the AMS was probably not detecting significant amounts of sodium nitrate. This is expected since the AMS vaporizer temperature was 550 C which is not high enough to volatilize sodium nitrate. On average for the entire study, the AMS nitrate and PILS nitrate were not well correlated, implying that the two methods were not detecting the same species. The study average ammonium to sulfate mole ratio is 1.5 +/- 0.2 from the data shown in Figure 2 and is 1.7 +/- 0.3 from the submicron impactor data (Bates et al., 2005). Since this ratio is less

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than 2, the submicron particles were acidic and should contain very little ammonium nitrate. Along with the high 30/46 ratio, this evidence supports the possibility that the AMS nitrate signal could be due to some other species and is the reason we included m/z 30 in the organic cluster analysis. This is now explained in the revised manuscript.

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?

Response: We agree that we focused on the benefits of HCA and did not mention its limitations in this section. We have improved this in the revised manuscript. We also mentioned that further information about category 1 might be obtained if the criteria for combining spectra were not as strict.

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.

Response: In the conclusion, we describe the value for the biogenic organic aerosol mass as the one derived by adding the contributions of categories 2-5 together and not as the true number. We agree with the reviewer that a complete proof can not be achieved at this stage.

Page 4620, line 17: The scientific context and applicability of the conclusions need to

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be stated. The current text is very technical in nature and does not properly cover the original objectives of the article.

Response: We add a sentence to highlight the benefits of HCA.

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.

Response: We have added to Table 2 numbers that show the deviations for the individual peak. The overall variability is given by the stopping condition that was used.

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.

Response: It is not possible to indicate variability within the bins in Figures 8, 9, 10 and 13 since the HCA only leads to one number for every bin and we generated only one set of HCA categories. Running the cluster analysis with different stopping conditions could lead to different categories.

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