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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 #4

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Overall, most of the points raised in the review were satisfactorily addressed. However, in my opinion, a small number of important issues still remain to be resolved, which are described below and I would suggest that the authors consider these further.

S1931: 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.

Referee: If the subtraction and clipping were of no ultimate benefit, then it begs the question of why they were employed in generating the results presented. Without a scientific basis, they only serve to weaken the paper.

S1933: 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 over-compensated by the assumption that all of category 1 is anthropogenic.

Referee: If, as stated, the authors believe that this bias is overcompensated, the evidence supporting this assertion must be shown, as it profoundly affects the validity of later sections of the paper.

S1933: Repartitioning will also occur on timescales longer than 1 minute between air masses that mix.

Referee: If the authors are arguing that during the low divergence periods, the air-masses were well-mixed and homogeneous enough that very little variations in the aerosol composition were observed within the 1-hour timescales, then it is this that should be stated. To reiterate my original point; there is absolutely no way that the AMS can detect any form of repartitioning between particles of detectable sizes. The instrument will report exactly the same mass spectrum for a given combination of components completely irrespective of their mixing state.

S1933: When the organic mass was less than 2 microgram/m3, the mass spectra were obtained from roughly 100 particles.

Do the authors mean 100 particles per mass spectrum or per peak? This is important because as the AMS used a quadrupole, 1 particle can only contribute to 1 random peak out of 300, so 100-particle mass spectra will be massively variable. 100 detected

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particles over 1 minute also corresponds to an incredibly low ambient concentration for a surface measurement (<5 p/cc by my calculations).

S1937: 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.

Referee: Observing something later in the day does not on its own prove it has undergone more photochemical processing since precursor emission. To make the statement that changes in the amount of processing were responsible for the changes in composition observed, a more thorough analysis of the airmass histories must be performed. As a bare minimum, the authors should at least estimate the approximate time since precursor emission. The authors must also be able to show that the initial precursor concentrations were sufficiently invariant between the different cases as well.

S1939: 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.

Referee: A scatter plot should still be possible if the gas phase calculation is averaged to the 1-hour time resolution of the AMS. If there are reasons why the two techniques disagree at times (in particular, during the case study explored in figure 11), these should be discussed as appropriate. A systematic comparison of the two techniques, even if the agreement is not perfect, would greatly strengthen the conclusions of this

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paper.

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