Atmos. Chem. Phys. Discuss., 6, S5049–S5052, 2006
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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.

**C. Marcolli et al.**

Received and published: 5 December 2006

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.

Response: we first preprocessed the spectra, including the subtraction and zeroing, and then performed the clustering in different ways (log and linear). The paper presents the clustering that we considered as the most interesting one (note that we generated our clusters before the reference spectra became available). While we think that the subtraction of the average noise level is beneficial when the high masses are given



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more weight (e.g. when using the log of the signal for the cluster analysis), we can not find any reason why this procedure should harm the cluster analysis when the linear signal is used. We add the following sentence to the paper: Although there could be a bias due to this procedure, it would occur mainly in the high m/z peaks where the signals were small and does not significantly impact the cluster analysis using linear signals.

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.

Response: we will change this part of the discussion, since in the meantime new reference spectra of isoprene oxidation products have become available. One of these spectra shows a very high correlation with category 2. This reinforces the conclusion that category 2 is biogenic. Also, category 1 shows a strong correlation with isoprene oxidation products, making our point stronger that category 1 is partly biogenic.

Referee: If the authors are arguing that during the low divergence periods, the airmasses 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 particles over 1 minute also corresponds to an incredibly low ambient concentration for a surface measurement ($<$5 p/cc by my calculations).



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Response: We measured the actual particle number concentration with a TSI CPC (model #3022A with a 50% lower cutpoint size of 7 nm) and found that it averaged 6500 p/cc and 3400 p/cc during high and low organic mass concentrations, respectively. This translates into roughly 100 particles per m/z per AMS mass spectrum during low organic mass periods. Since it is typically observed that about 2% of the ambient particles contain 50% of the particle mass (Bahreini et al., 2003), the resulting mass spectra might nevertheless be influenced by counting statistics. We therefore think that some of the 1-spectrum-clusters are indeed due to this effect. Because such clusters were absent for high organic mass loadings, we hypothesize in the manuscript that during these time periods, the air masses are well internally mixed. We will make this clearer in the revised manuscript.

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.

Response: Unfortunately, the HYSPLIT back trajectories are inconsistent with the gas phase, aerosol, and wind field measurements for this time period and location. For example, the data from the night shows high monoterpene concentrations and the measured surface winds were from the north (see Figure 13 in de Gouw et al., 2005). Hence, the data indicates that the monoterpenes left the coast at night and were not exposed to sunlight prior to sampling. In contrast, the back trajectories for the same time period indicate that the air mass came from the east and spent some time in sunlight from the previous afternoon prior to sampling. If this were true, the monoterpene concentrations should be relatively low. As the day progressed, the measured surface winds were northeasterly and the monoterpene concentrations decreased after



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sunrise (around 1000 UTC). The isoprene source term remained high for a few hours (from 1000 to 1500 UTC), but the isoprene concentrations decreased like the monoterpenes. This is consistent if these species react with sunlight while over the water. Yet the back trajectories indicate that the air mass was above the continental nocturnal boundary layer and should not contain any photochemically-active biogenic species.

We added this to the manuscript: Shipboard measurements from 1000 to 1500 UTC indicate that the surface winds were from the same direction after sunrise, the wind speeds were approximately 5 knots, the ship moved much more slowly, and its track roughly paralleled the coast where the emissions were relatively constant. Hence, the time since emission for the air mass sampled from 1000 to 1500 UTC was approximately 6 hours. Therefore, the air sampled had left the coast during the night and was exposed to increasing levels of sunlight as the day progressed.

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 paper.

Response: We now have a scatter plot in the paper.

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