Atmos. Chem. Phys. Discuss., 6, S5053–S5056, 2006
www.atmos-chem-phys-discuss.net/6/S5053/2006/

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: 5 December 2006

We thank the referee for his/her positive feedback.

Response to general comments:

The paper by Marcolli et al. applies cluster analysis to data collected by an Aerodyne Aerosol Mass Spectrometer (AMS) on a ship cruise off the coast of New England during the New England Air quality study (2002). I understand this manuscript as an explorative, methodological study, which tries to categorize the potential origin and folded, the chemical processing of the organic aerosol component. It is another impor-

tant attempt to get hold on the complex organic matrix in particulates before detailed speciation. Moreover, the organic matrix in this case is represented by broken down fragment patterns for experimental reasons. The message of the paper is twofold, the analysis succeeded with some certainty, e.g. in attributing biogenic origin to categories 3-5. The analysis "failed", because it could not resolve the issue of anthropogenic vs. biogenic for the most abundant category 1. Based on the explorative and methodological aspects, I think this is an excellent paper, which is carefully written. It surely brings the treatment of the organic particulates methodologically forward. It could be published in ACP as it is, but the many suggestions made already by the co-referees will clearly improve is already very good manuscript.

Would it possible to find subcategories within category 1 by analyzing certain smaller m/z ranges, e.g. m/z $>$ 90, or m/z around 44 etc.?

Response: We attempted a cluster analysis of the whole dataset for the organic masses with m/z $>$ 50. This led to a similar result as the cluster analysis with all organic masses: we obtained one main category and several smaller ones. However, the categories seemed to be less specific for particular events or situations. We therefore concluded that the higher mass peaks seemed to carry rather less information than the masses with m/z $<$ 50 due to more noise and less signal in these channels for the conditions and sensitivity of this instrument. To find subcategories within category 1, the category 1 spectra or the whole dataset could be clustered with a stricter stopping criterion, leading to more clusters and at some stage also to a splitting of the category 1 spectra into two or several clusters. However, distinct clusters may not readily form if the data contain a continuum of different compositions as has been observed with single particle data for mixed sulfate/carbonaceous particles.

p. 4614 line 3ff. It looks as if cat. 4,5 basically represent ozonolysis products of biogenic emissions. Since obviously these are also formed during dark, they arise supposedly from plants that have pools and substances which are stored in pools, thus monoterpenes?

ACPD
6, S5053–S5056, 2006

Response: Categories 4 and 5 indeed show the highest spectral correlations with alpha-pinene oxidation products in the presence of OH and O3, respectively. Especially category 5 is not abundant at high solar irradiance and typically peaks in the morning. This is all consistent with category 5 (and maybe also category 4) originating from monoterpene ozonolysis. The data shown in Figure 11 are from a case study where there were high monoterpene emissions and low ozone concentrations (around 20 ppbv). If indeed a fraction of the SOA during this period is due to alpha-pinene oxidation, this may indicate that the formation is monoterpene-limited rather than ozone-limited.

p.4614 line 17 and p.4616 line 6 How certain is the categorization of aerosol components as anthropogenic via isopropylnitrate? If the isopropylnitrate argument fails, is then the sum of evidence still sufficient that cat. 1 and total organic mass arise mostly from anthropogenic origin?

Response: We will add correlations with further reference spectra to the revised manuscript, showing that category 1 also correlates fairly well with isoprene oxidation products in the presence of high NOx levels. This reinforces the conclusion that organic mass from biogenic sources also contributes to category 1. The correlation of the organic mass with isopropylnitrate might also indicate that anthropogenic pollution augments the oxidation of organic material originated from biogenic species. With the evidence at hand, we consider both, high or low biogenic contributions to category 1 as possible. What is clear is that anthropogenic pollution causes an increase in organic mass.

p. 4614 line 23 What exactly is meaned by "secondary anthropogenic processes"?

Response: A definition is added that secondary anthropogenic processes refer to reactions involving either biogenic or anthropogenic VOCs with secondary anthropogenic oxidants (ozone or nitrate radical) or with hydroxyl radical in the presence of high nitrogen oxide concentrations.

ACPD
6, S5053–S5056, 2006

EGU

p.4618 line 21 The organic nitrate argument is vague. There are significant contributions to m/z30 in SOA formation in total absence of NOX and NOY.

Response: We have added more about m/z 30 to the beginning of that section.

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