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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Temperature-dependent accumulation mode particle and cloud nuclei concentrations from biogenic sources during WACS 2010" *by* L. Ahlm et al.

L. Ahlm et al.

lars.ahlm@itm.su.se

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Response to reviewer 2

We thank reviewer #2 for comments and suggestions for improvement of our manuscript. The comments from the reviewer followed by our responses to the comments can be seen below. In the updated manuscript, changes have been marked in red color.

Comment #1.

It is not clear that the four periods categorized by Macdonald et at. (2012) are defini-

tive for discerning influences of various sources to the siteâĂŤwhich seems to be one of the main objective of this manuscriptâĂŤand a separate set of indicators for source influence (e.g., temperature) are described in various places throughout the text. For instance, Periods 2 and 4 are very similar with respect to the aerosol/gas-phase measurements, while Period 2 is actually comprises two periods relevant for chemical interpretation (anthropogenically dominated vs biogenically dominated). As such, this manuscript would be strengthened by a contingency table showing the relationship between the periods from Macdonald et al. (2012) and periods outlined in the first two bullet points in Section 4. There are statements in the manuscript to the effect that Period 4 has some biomass burning events, but is not borne out by many of the analysis presented in the manuscript (e.g., the PMF analysis on FTIR spectra or STXM/NEXAFS analysis), so it seems this complexity can be neglected (to a first order) in presenting this information.

Response:

We have added temperature to Figure 2 in order to make the dependence between temperature, VOCs and the biogenic PMF factors clearer, and to clearer illustrate differences between the four periods. We have also added relative humidity to Figure 2. We are not sure what the reviewer means with "period 2 actually comprises two periods relevant for chemical interpretation (anthropogenically dominated vs biogenically dominated)". Period 2 was to a very large extent dominated by biogenic sources with low impacts from anthropogenic sources. It is true that period 2 and period 4 are similar in terms of meteorology. However, the reason that we chose to keep these two periods separated is that (as the reviewer mentions) period 4 had impact from biomass burning (apart from biogenic sources). Period 3 is different from all other periods in that it is colder than period 2 and period 4 but warmer than period 1, and this period has higher influence from combustion sources than period 2 and 4. Period 1 is much colder than the other periods and has much lower impact from biogenic sources than the other periods. Therefore, we think the manuscript gains from the division of the

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measurement campaign into four periods. Acetonitrile data and biomass burning will be presented in the overview paper by Macdonald et al. (which is just about to being submitted), why we prefer to not show those results here. However, we mention in the end of Sect. 3.1 that the influence of biomass burning during period 4 could be observed as elevated acetonitrile concentrations. We have now also added that black carbon concentrations were considerably higher during period 4 than any other period. The authors are not sure what the reviewer means by a "contingency table." We think what is meant is a mapping between the periods described by Macdonald et al. and the periods described here. However, the periods used in both tables are identical (which we have now stated explicitly) so there is no need to show the relationship in such a table.

Comment #2.

Regarding correlations of PMF factors with particle number concentrations, one interpretation which is not stated explicitly is that during biogenic-aerosol dominated periods, most of the accumulation-mode organic particles are biogenic, whereas this is not necessarily the case during combustion source-influenced periods (presumably because there is OM from biogenic sources mixed in).

Response:

We think the reviewer is noting correctly that there is also biogenic-aerosol during the combustion periods, as indicated by the PMF factors. In other words, the "dirty" periods also have some "clean" aerosol present, we are just singling out the clean periods as being dominated by biogenic. We have added a statement to clarify this in the manuscript.

Comment #3.

I can appreciate that the authors derive the source class based on correlations with XRF elemental composition and other measurements without consideration for spec-

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troscopic signature, but the significant departure in factor profiles from previous assignments for similar source classes (Schwartz et al., 2010; Takahama et al., 2011; Russell et al., 2011) should be noted. Even the variability in quantified functional group abundance between the two sites is significantly different, especially with respect to the carbonyl and carboxylic acid fractions (Factors C and D) (the profiles look quite similar but can this quantification be correct?). This seems to be inconsistent with the conclusions of Russell et al. (2011) regarding broad similarities in composition among PMF profiles attributed to common sources classes.

Response:

The reviewer is correct in that the quantified functional group abundances are significantly different between the two sites for factors C and D. Both factor C and factor D agree well between the two sites for alkane and alcohol functional groups, but when it comes to acid versus non-acid carbonyl, factor C at WHI matches better with factor D at WRN, and contrary for factor D at WHI and factor C at WRN. It seems that PMF did not succeed in completely separating the two factors from each other. All the paper, except Fig. 4 and Tables 1a-b, handle the two biogenic factors as one combined biogenic factor. Therefore we do not see any reason for handling the two factors separately in Fig. 4 and Tables 1-b, and we now instead present one combined biogenic factor in Fig. 4, and we present correlation coefficients for this combined factor in Tables 1a-b. This combined biogenic factor at WHI now matches relatively well with the corresponding factor at WRN in functional group contributions. The non-acid carbonyl contribution to this factor (17-19%) now also matches the combined biogenic factor in Schwartz et al. (2010) where the non-acid carbonyl fraction was 16%. When it comes to the other factors, the combustion factor spectra resemble the corresponding spectra in Schwartz et al. (2010) and Takahama et al. (2011) (which is already noted). The detritus factor spectra resemble the detritus factor spectrum in Liu et al. (2012) (and the spectrum of the “Biogenic Factor Part 1 from Whistler mid-valley study” shown by Takahama et al. (2011)).

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Comment #4.

Why was FPEAK=0 chosen in both cases (Figure 3)? Is there another interpretation of the factor analytic decomposition that would make more sense? It is not clear if these correspond to the minimum value of the objective function, but as discussed by Paatero et al. (2002), the rotations performed by PMF are approximate and some amount of increase in Q-value is acceptable among alternate solutions generated by the algorithm.

Response:

The minimum of the Q/Qexpected appeared at FPEAK=0 (Whistler Peak) and close to FPEAK=0 (Raven's Nest) (Fig. 3). The differences in spectra between different solutions for values of FPEAK close to zero were small. Therefore we chose the solutions for FPEAK=0.

Comment #5.

p. 28004, lines 16-18: The wording is not entirely correct in interpreting single-particle measurements. The alkene/aromatic groups were not "attributed [...] to the influence of carbon tarballs," but they indicated that the selected particles examined were tarballs observed in biomass burning episodes, as reported previously by Tivanski et al. (2007).

Response:

Thank you. We have changed that now.

Comment #6.

p.28008, second paragraph: The authors draw upon correlations between number concentrations of particles less than 100 nm and a particular PMF factor to support their assignment of this factor to a predominantly combustion source. As these nucleation mode particles (likely to be largely BC in composition) are probably not the particles measured by FTIR, the authors should include available citations to studies showing

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the mass size distribution of OM from combustion sources in the accumulation mode - which is what is presumably measured by their FTIRâĂŤto make this argument more convincing.

Response:

We have added the reference “Kittelson, D. B.: Engines and nanoparticles: A review, J. Aerosol Sci., 29, 575-588, 1998”.

Comment #7.

There is some mention of periods during which the WRN and WHI measurements are decoupled because of boundary layer meteorology. Would not the manuscript provide additional contributions to the community by focusing on differences in aerosol composition below and above the boundary layer, if such distinction can be made from archived meteorology (e.g., HYSPLIT), remote sensing information (McKendry et al., 2011), and the suite of in-situ instruments at the sites?

Response:

Both the two sites were temporarily decoupled from the boundary layer during the cold period 1, which implies that it is not possible to make a comparison between the boundary layer and free tropospheric aerosol. Furthermore, during this period the two sites were frequently in cloud. During the other three periods the mixed layer grew well above Whistler Peak in the afternoons which means that sampling was performed either in the residual layer or in the mixed layer. Even if the Whistler Peak site temporarily would have been located in the free troposphere the FTIR filters were sampled over 24 hours, so it is not be possible to extract those periods.

Comment #8.

Figure 6: The top spectra seem to include some saturated spectra.

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The individual spectra are not saturated even though the tops of the bars may look like they could be. The average spectrum in the top panel of Fig. 6 was obtained from four different spectra. If we remove one of these spectra, the variability in the top panel is reduced to a large extent.

Comment #9.

Figure 8: Would it make sense to segregate the profiles based on either the periods 1-4, or combustion and biogenic source-dominated periods? It is difficult to assess the relative contributions from the different source classes otherwise (e.g., is this diurnal profile in BC at the site observed during biogenically-dominated periods).

Response:

It was first our intention to include diurnal cycles for all the four periods. However, we decided that it was not a good idea statistically to present average diurnal cycles over periods that are only a few days – like period 2 and period 4. The reviewer's suggestion of only separating the campaign in two periods, anthropogenic and biogenic source-dominated periods, is not possible here because period 4 (which is influenced both by biogenic sources and biomass burning) is the period that differs the most from the other periods in that is has considerably higher concentrations and clearer peaks in black carbon than the other periods. Hence, there are more factors than only biogenics vs anthropogenic to consider here. The reason that we chose to show diurnal cycles for period 3 is that there were very clear anabatic flows during daytime and katabatic flows at nighttime that we thought represented a good case study. The average diurnal cycle for period 2 had BC peaks at the same times as period 3. However, these peaks were less pronounced and lower in concentration in period 2 than in period 3.

Comment #10.

Figure 10: What is implied by the linear model (as indicated by regression lines) between number concentration and temperature? Related to a comment by the other

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reviewer, as correlation coefficients indicate the degree of linear relationship, they are not often the ideal metrics to use in environmental analysis–though indeed they are widely applied out of convenience. However, correlations can be useful to examine relationships provided that the degree of nonlinearity is small, or the dynamic range is small enough that the functional relationship can be approximated with a linear one. But fitting a linear model suggests a stronger interpretationâĂŤwhat physical significance do the slopes and intercepts have?.

Response:

We think that the relations in Fig. 10 seem linear enough (according to the plots) to motivate an investigation of the linear correlations. Perhaps we would obtain even higher correlations by assuming an exponential dependence for Fig. 10a-b, but we think that the linear correlations are strong enough to show that there is a clear dependence on temperature at both sites. With the slopes and intercepts presented in Fig. 10, we can to some degree predict the CCN and accumulation mode number concentrations during this campaign in Whistler. It is possible that the slopes and intercepts are only relevant for this campaign in Whistler. However, by presenting these equations it will be possible to compare these with relations obtained at other sites which might help in obtaining a more complete picture of the biogenic SOA contribution to CCN concentrations.

Interactive comment on Atmos. Chem. Phys. Discuss., 12, 27989, 2012.