

Interactive
Comment

Interactive comment on “Long-term volatility measurements of submicron atmospheric aerosol in Hyytiälä, Finland” by S. A. K. Häkkinen et al.

Anonymous Referee #3

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This manuscript presents long-term measurements of atmospheric aerosol volatility in a forested site in Finland. A volatility differential mobility particle sizer (VDMPS) is used together with a twin-DMPS to measure aerosol mass fraction remaining (MFR) as a function of VDMPS operating temperature. Trends in the MFR are interpreted by comparisons with other data including black carbon measurements from an aetholometer, various environmental and meteorological variables, and AMS non-refractory aerosol composition measurements. A significant correlation between MFR and black carbon mass fraction is observed for all seasons except summer. Correlation between MFR and anthropogenic tracers such as CO, SO₂, and NO_x as well poly-aromatic hydrocarbons (PAH) are used to suggest a connection between non-BC MFR and anthropogenic influences. Correlations between non-BC MFR and aerosol organic and nitrate content observed in clean forest-influenced air during fall is used to suggest the

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existence of low volatility organic nitrates in the aerosol.

The paper is well written and the measurements provided are of interest, particularly since they cover a long time period and several seasons. The interpretation of the data, however, requires presentation of more supporting details and analysis and I recommend that this manuscript be published after the specific issues raised below are appropriately addressed.

Major Comment

1) The volatility measurements only apply to a limited particle size range (20-500 nm), but these measurements are correlated with BC and AMS measurements which cover a larger size range. The authors should provide a more detailed explanation of why these correlations can be done without correcting the BC and AMS measurements for these differences first. For BC the authors should use current or previous measurements to quantify or estimate the mass fraction of BC that is in the 20-500 nm range. For AMS, this is even more important because it is expected that a significant fraction of the sulfate and organic mass will be in particles larger than 500 nm. Moreover, chemical composition is likely size dependent as well. Since no attempt is made to correct for these effects, it is not clear whether observed correlations are simply driven by size dependent differences in particle composition or real composition dependence of MFR. The AMS is capable of providing both mass spectra and size distributions. So, the chemically speciated size distributions can be used to calculate species mass concentrations over the relevant size range. This would provide a more easily interpretable and direct correlation between particle composition and MFR.

2) A key conclusion of this manuscript is that organic nitrates may account for MFR obtained in the fall time period when sampled air was clean and advected over forests. The suggestion of organic nitrate is made based on the fact that all the nitrate is not neutralized by ammonium and the 46/30 ion ratio. More details should be given to substantiate this conclusion. For example, In figure 9 a high degree of correlation

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between MFR at high temperature is observed not only for organic and nitrate but also chloride. Is it possible that both the nitrate and chloride are inorganic in nature (NaNO_3 , CaNO_3 ..)? The authors should discuss this and also present the observed 46/30 ratios. The size distributions of the nitrate and chloride aerosol components would also be very useful in understanding their possible sources. If these were indeed organic nitrates, are they likely to survive the thermal denuder temperatures or would they decompose at 280 deg C?

Other Comments

1) Throughout the manuscript the authors switch between using "MFR" and "non-volatile particle fraction". The former term is less confusing so I suggest that the authors only use MFR in the entire manuscript and limit the use of the latter term. Also, please be consistent in using the non-BC subscript whenever appropriate. For example, I think section 4.4 deals with non-BC MFR so the title of this section should contain this subscript.

2) Page 11212, line 12: Please explain where the assumed particle density value comes from. Is the density that is used consistent with the known composition of the aerosol? Also, one would expect the particle density to change as a function of thermal denuder temperature. How much error does this introduce in the MFR?

3) p. 11216, last sentence: "Over the whole measurements period the non-volatile particle mass was higher at lower temperatures". Do the authors mean non-BC MFR or total MFR here? In any case, this statement seems counter-intuitive to me. At lower temperatures, more volatile species should condense. So, the non-volatile mass fraction should go down instead of up. Is the non-volatile mass that correlates with the lower temperatures BC or non-BC related? If it is BC related perhaps it reflects BC sources such as home heating. A more detailed discussion of these possibilities would be useful

4) Figure 6. Why is the correlation coefficient between MFR and BCF so much lower

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than that observed in the spring when much of the winter MFR is due to BC?

5) Figure 7. Since the authors discuss the possibility of organic nitrate, it would be useful if they shaded the nitrate wedges in the pie charts to reflect the portion that is estimated to be due to NH_4NO_3 and the portion that is not neutralized.

6) Figure 10. Why not show the corresponding windroses for spring so that the readers can see a contrast as in figure 7.

7) section 4.4 discussion. Can the campaign backtrajectories be used to estimate an approximate photochemical age metric of the measured airmasses? If so, it would be interesting to see how the non-BC MFR correlates with age.

Interactive comment on Atmos. Chem. Phys. Discuss., 12, 11201, 2012.

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