

**Answers to referee #3 comments: "Long-term volatility measurements of submicron atmospheric aerosol in Hyytiälä, Finland" by S.A.K. Häkkinen et al., 2012.**

Answers to Anonymous Referee #3

*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 aethalometer, 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, SO<sub>2</sub>, and NO<sub>x</sub> 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 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 comments*

*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.*

For the BC analysis see answer to comment #8 by referee #1.

In the analysis the AMS size range was considered to be roughly comparable with that of the VDMPS. The AMS measurement size range, using the standard aerodynamic lens, is estimated to reach 600 nm (50% detection efficiency cut point), based on study by Liu et al. (2007, AST). Based on this, and the observation that the AMS mass in Hyytiälä correlated best with DMPS size range of 0-600 nm, the AMS data is corrected for collection efficiency to be comparable with DMPS derived mass in size range 3-600 nm. We admit the difference between the cut size of 500 nm of VDMPS and 600 nm of AMS will, at some occasions, when there is a large particle mode present in the 500-600 nm size range, cause a discrepancy between the two measurements, adding to the error margin of the analysis, but at this point we have few tools to address the problem in a proper fashion. This is because we do not have AMS size separated data available for the measurements described here, owing to technical and data inversion problems with the triggering of the size measurement and the short PToF chamber of the AMS variant used in this study. Therefore we have no specific information on the size dependent distribution of the different chemical species available, and cannot

say if the particles in size range 500-600 nm are different from the particles below these sizes. We will add the size range of AMS measurements to the revised manuscript.

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 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<sub>3</sub>, CaNO<sub>3</sub>..)? 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?*

The mass loadings of chlorides observed by the AMS suggest that the amount of chloride compounds is almost negligible in Hyytiälä, and the amounts observed are most likely insufficient to have any effect on the total MFR, within the measurement inaccuracies. Thus, even if all the chlorides seen were in the form of NaNO<sub>3</sub>, the amount of nitrate it would bind would not make much of a difference in the grand scale, as the mass loadings of nitrates is generally around 20 –fold that of chlorides. This is why we feel chlorides are not playing a big role in figuring out which form the nitrate is in. The question is still valid and we will add a mention of this. The size distribution data is unfortunately not available, for reasons described in the answer to your comment #1.

We will present the 46/30 ratios (Appendix A, Fig. 1A, lower panel) (see Fig. 3.1, lower panel). Unfortunately, we have been unable to find many published articles on the use of the 46/30 ratio, even if it is very often used as a tracer for inorganic nitrate. As for the behavior of organic nitrates, at this point we have been able to find little published information on their phase of form (e.g. if they may take part in salt or polymer formation), and are at this point unable to conclude how they would behave in high temperatures.

#### *Other Comments*

1) *Throughout the manuscript the authors switch between using "MFR" and "nonvolatile 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.*

The section 4.4 should have MFR(non-BC) in the title. We will make sure that the MFR and MFR(non-BC) are consistently used throughout the text.

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?*

According to Kannosto et al. (2005) the density of accumulation mode aerosol particles in a boreal forest environment is in the range of 1.1-2 g cm<sup>-3</sup>. We assumed the density to be in the middle of the presented values, thus 1.6 g cm<sup>-3</sup>. Particle density will change when the chemical composition changes and the uncertainty due to change in particle chemical will most probably increase with increasing heating

temperature. If the density of the residual after the heating is higher than the density of the ambient particle, the MFR will increase and vice versa. E.g. if the density of the residual is  $1.8 \text{ g cm}^{-3}$  (BC density, McMeeking et al., 2010) there would be 13% increase in the MFR presented in our study. If the density of the residual is low e.g.  $1 \text{ g cm}^{-3}$  there would be 38% decrease in the MFR. We will add explanation of the particle density choice and uncertainty estimation of MFR at  $280 \text{ }^\circ\text{C}$  due to density change to the revised manuscript.

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.*

We mean MFR(non-BC) when presenting correlations with meteorological parameters. However, there was also a significant correlation between ambient temperature and MFR ( $r = 0.61$ ,  $p\text{-value} < 10^{-5}$ ). Therefore, it seems that the correlation between aerosol residual and ambient temperature is both BC and non-BC related. It seems that aerosol and vapor sources are important in explaining the observed correlation. As you pointed out the observed correlation can be due to anthropogenic emissions e.g. from residential heating. Even though there is more volatile material condensing on aerosol particles in colder temperatures, also chemistry-related processes may affect the volatilities of condensing compounds in the particulate phase. However, that is something we can only speculate. We will add more discussion on this topic to the revised manuscript.

4) Figure 6. *Why is the correlation coefficient between MFR and BCF so much lower than that observed in the spring when much of the winter MFR is due to BC?*

During winter and fall periods the mass fraction of BC in submicron aerosol particles (BCF) was the highest. Also the MFR was the highest during these seasons. However, the mass fraction of BC in the non-volatile residual (at  $280 \text{ }^\circ\text{C}$  with a residence time of 1.2 s) was the highest during summer and fall (68%). During winter BC explained around 55% of the non-volatile mass and during spring 57%. This may affect the observed correlation between BCF and MFR. We will clarify Section 4.3 concerning this subject in the revised manuscript.

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  $\text{NH}_4\text{NO}_3$  and the portion that is not neutralized.*

When estimating the partition of inorganic and organic nitrate we found the average contribution of inorganic nitrate (ammonium nitrate) was below 1% both during spring and during fall (max 2%) and thus almost all AMS-nitrate was from organic origin. We will make a figure showing the inorganic nitrate and organic nitrate wedges (Appendix A, Fig. 1A, upper panel) (see Fig. 3.1, upper panel).

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

We will show the windroses for spring 2008 for comparison (Appendix A, Fig. 2A) (see Fig. 3.2)

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.*

We investigated the aging of the aerosol by determining the cumulative radiation aerosol is exposed to when travelling to Hyytiälä. We used sun flux data provided by HYSPLIT model which calculated the air mass trajectories 96 hours backwards. Cumulative radiation was correlated with the MFR(non-BC) and a weak negative correlation was found ( $r = -0.30$  and  $p\text{-value} < 10^{-5}$ ) (see Fig. 3.3). This finding is similar to the correlation we observed between MFR(non-BC) and global radiation ( $r = -0.27$  and  $p\text{-value} < 10^{-5}$ ). It seems that aerosol particles are more low-volatile when there is less aging i.e. exposure to sun radiation. However, no strong conclusions can be made about the effect of aerosol aging on aerosol volatility.

#### References:

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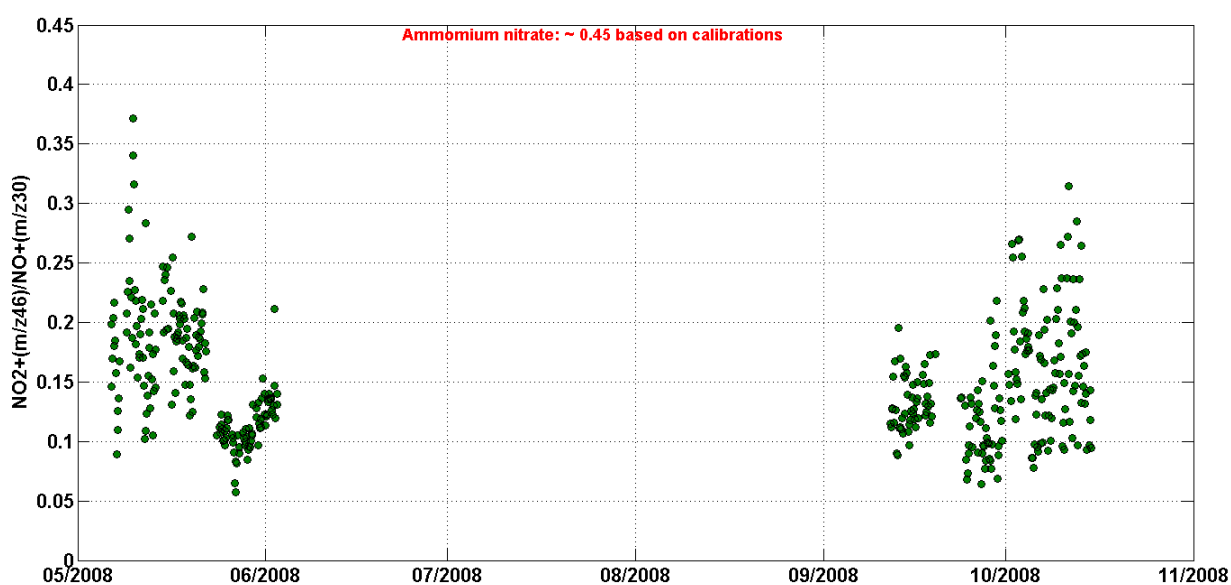
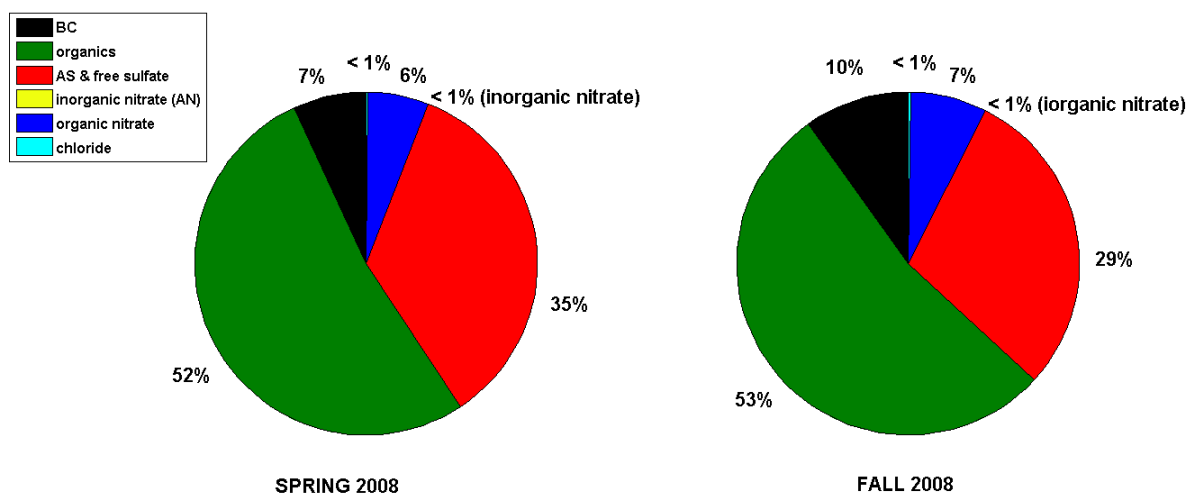


Fig. 3.1 Aerosol chemical composition during AMS measurement campaigns in spring and fall 2008 is illustrated in the upper panel. Ammonium has been divided to sulfate and nitrate to form ammonium sulfate (AS) and ammonium nitrate (AN). Nitrate that is not neutralized by ammonium is assumed to be organic nitrate. In the lower panel  $\text{NO}_2^+/\text{NO}^+$ -ratio time series from spring and fall campaigns are presented. This ion-ratio describes qualitatively the relation between inorganic and organic nitrate (Fry et al., 2009). According to AMS-calibrations ammonium nitrate ion-ratio is around 0.45. Ion-ratios smaller than this suggest the presence of organic nitrates.

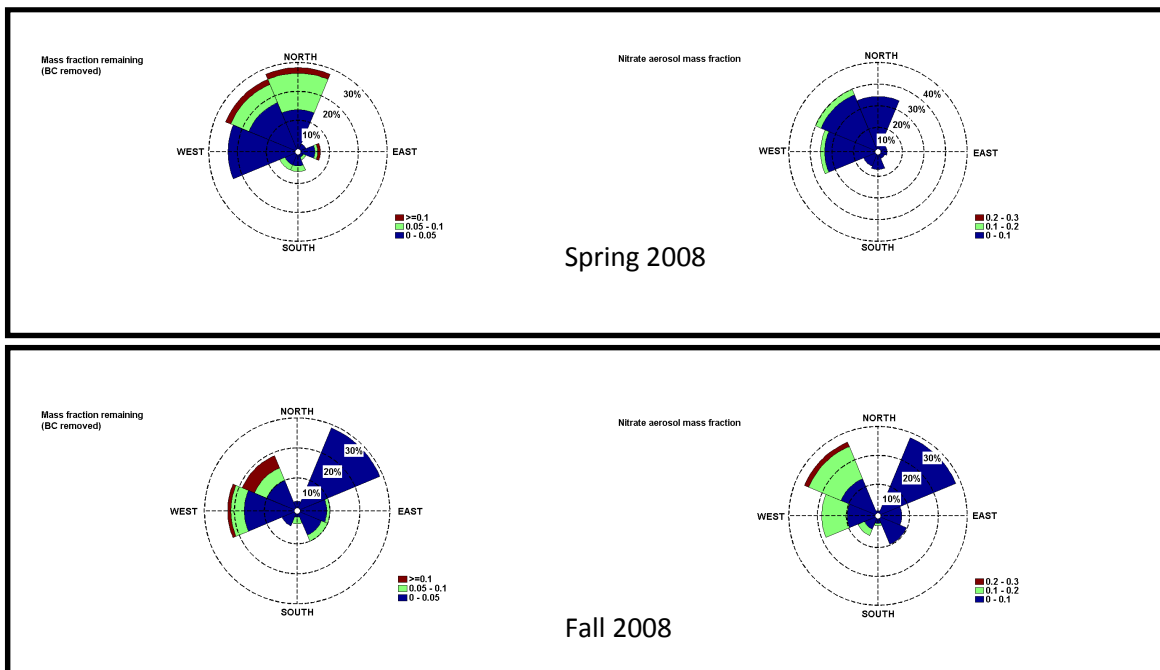


Fig. 3.2 Wind roses of aerosol mass fraction remaining (non-BC) after heating to 280 °C and nitrate mass fraction during AMS measurement campaign in spring 2008 (upper panel) and similar figure for campaign in fall 2008 (lower panel). The colors represent the mass fractions, and the percent values correspond to the amount of data from each direction bin. In fall 2008 aerosol nitrate mass fraction and  $MFR_{\text{non-BC}}$  are correlating.

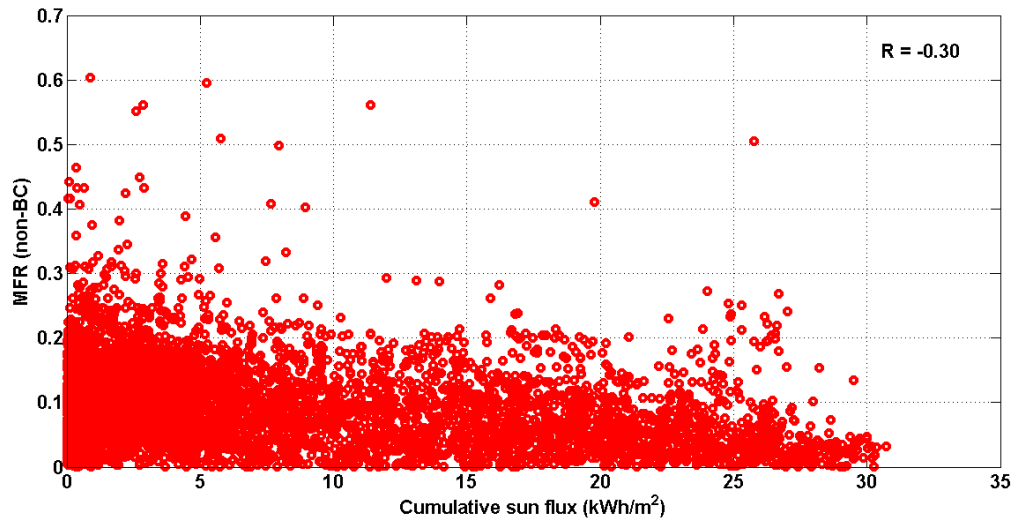


Fig. 3.3 MFR(non-BC) as a function of cumulative sun flux determined from data produced by backtrajectory model HYSPLIT. Correlation coefficient is provided in the figure.