Answers to referee #2 comments: "Long-term volatility measurements of submicron atmospheric aerosol in Hyytiälä, Finland" by S.A.K. Häkkinen et al., 2012.

Answers to Anonymous Referee #2

The paper describes field measurements of aerosol volatility and other parameters over a time period of more than two years. Seasonal trends of aerosol mass fraction remaining (MFR) at different temperatures are presented. From black carbon measurements and the aerosol MFR measured at 280 ºC the authors determine the very low-volatility fraction of organic aerosol. From a correlation analysis with AMS and trace gas data a source apportionment of this low volatility organic fraction was performed. The determination of the aerosol mass fraction remaining was done the following way. Ambient aerosol was directed through a heated thermodenuder and the remaining particle mass distribution was measured with a DMPS from 20-500 nm. The reference point was another DMPS, which measured the aerosols without treatment in a range from 3-1000 nm. The mass fraction remaining is then given by the ratio of the measured aerosol mass from the two DMPS within the same aerosol diameter range of 20-500 nm (equation 3). As seen from Figure 3 there is a very large aerosol mass fraction with diameter larger than 500 nm. This means that all particles larger than 500 nm will also partly evaporate in the thermodenuder and some will shrink to sizes below 500 nm. Thus, equation 3 is by no means the true aerosol mass fraction remaining. Therefore, the analysis in this paper is based on a flawed approach and all correlations or apparently observed effects might be artifacts. Even for the MFR at 280 ºC we cannot be sure if a fraction of still relative volatile material from very large particles, that did not have time to completely evaporate, contribute to the so-called non-volatile MFR(non-BC). For this reason I cannot support the publication of this paper as it is.

Your comment concerning the size discrepancy between DMPS and VDMPS systems is relevant. The use of size range 20-500 nm for both DMPS and VDMPS data when determining the MFR was not properly discussed in the manuscript. In the following we explain why we used this size range in the first place and how the results would change if the size range of 20-1000 nm was also used for the VDMPS data. We will also revise the manuscript accordingly.

DMPS system used in Hyytiälä measured aerosol sizes up to 1 µm. This was ensured using PM1.0 inlet. However, VDMPS system measuring particles up to 1 µm did not have the same inlet and therefore once in a while VDMPS detected also particles that had original (non-heated) diameter of above 1 µm. Although there are not many coarse mode particles (around 10 cm^{-3}) in Hyytiälä, their effect on aerosol mass can sometimes be significant. We saw that these coarse mode particles measured with an aerodynamic particle sizer (APS) sometimes disturbed the VDMPS measurements and caused noise in the data at the larger end of particle sizes. In order to remove the noise from the VDMPS data, size range of 20-500 nm was selected. Determining the corresponding size range for DMPS is challenging. At low heating temperatures comparison between DMPS and VDMPS both in the size range of < 500 nm is valid. However, at high heating temperature such as 280 ºC more error will arise when using the same size range for DMPS and VDMPS. This is because it is probable that particles originally > 500 nm in diameter are detected with a VDMPS after heating. Due to this we recalculated the MFR using size range 20-500 nm for the VDMPS and 3-1000 nm for the DMPS. Thermogram based on these calculations is shown in Fig. 2.1 (panel A). These MFRs represent the absolute minimum non-volatile aerosol mass fraction. Even in this case there is a significant amount of very low-volatile material in submicron particles (MFR at 280 ºC is 15%), and the thermogram shows similar behavior within the experimental uncertainty. Including the VDMPS data from the whole 20-1000 nm size range, on the other hand, showed similar MFR values as the size ranges used in the manuscript at lower temperatures, but slightly higher values at 280 ºC (24% when the value presented in the manuscript is 19%). The values calculated for the < 1000 nm sizes in both DMPS and VDMPS represent the absolute

possible maximum value for the MFR, and the results strengthen our main conclusion on other material than BC explaining an important portion of the non-volatile residual.

We also repeated the whole correlation analysis presented in the manuscript using the recalculated MFR values (VDMPS < 500 nm and DMPS < 1000 nm as well as VDMPS and DMPS < 1000 nm) (see Table 2.1). For the VDMPS size range of 20-500 nm and DMPS size range of 3-1000 nm, the correlations with the investigated variables did not change significantly. For the < 1000 nm size range for both instruments (where the VDMPS data were disturbed by the noise from the coarse mode), the correlations with PAHs, temperature and global radiation with the fraction that does not evaporate at 280 ℃ exist, although not as strongly as with the size range chosen. Clear positive correlation (r = 0.80) between $MFR_{<1000nm}$ and $MFR_{<500nm}$, as shown in Fig. 2.2, indicates that even though there is noise in the $MFR_{<1000nm}$ data, the observed correlations are still representing real phenomena and are not caused by artifacts. For many of the trace gases, however, the correlations do disappear under the noise. For the comparison of AMS results with DMPS and VDMPS results, on the other hand, the selected size range of 20-500 nm for both DMPS and VDMPS used in the manuscript is reasonable since AMS do not measure effectively chemical composition of particles > 600 nm in size.

We will discuss the problems that arose in the VDMPS data analysis and clearly explain the reasons why the size range of 20-500 nm was used in the revised manuscript and remove the speculation on the correlation with the trace gas concentrations as it is possible that there the choice of the size range could have affected the correlation analysis.

Table 2.1 Correlation between MFR_{non-BC} (defined three different ways) and meteorological parameters: trace gas concentrations, ambient temperature, relative humidity, radiation, boundary layer height and total PAH mass fraction. Correlation coefficients (r) and p-values in brackets describing the significance of the meteorological correlation are from 24 h median data. For PAH correlation monthly averages were used.

|	MFR_{non-BC} VDMPS < 500 nm DMPS < 500 nm	MFR_{non-BC} VDMPS < 500 nm DMPS < 1000 nm	MFR_{non-BC} VDMPS < 1000 nm DMPS < 1000 nm
NO	$0.07\ (10^{-1})$	$0.09\ (10^{-2})$	$0.02\ (10^{-1})$
NO_x	$0.33\ (< 10^{-5})$	$0.35\ (< 10^{-5})$	$0.08\ (10^{-1})$
O_3	$0.06\ (10^{-1})$	$0.06\ (10^{-1})$	$0.06\ (10^{-1})$
SO_2	$0.44\ (< 10^{-5})$	$0.46\ (< 10^{-5})$	$0.15\ (10^{-4})$
H_2O	$-0.45\ (< 10^{-5})$	$-0.41\ (< 10^{-5})$	$-0.28\ (< 10^{-5})$
CO_2	$0.42\ (< 10^{-5})$	$0.44\ (< 10^{-5})$	$0.09\ (10^{-2})$
CO	$0.46\ (< 10^{-5})$	$0.47\ (< 10^{-5})$	$0.003\ (10^{0})$
RH	$0.18\ (< 10^{-5})$	$0.15\ (10^{-4})$	$0.05\ (10^{-1})$
Temperature	$-0.46\ (< 10^{-5})$	$-0.41\ (< 10^{-5})$	$-0.25\ (< 10^{-5})$
Global-radiation	$-0.27\ (< 10^{-5})$	$-0.22\ (< 10^{-5})$	$-0.22\ (< 10^{-5})$
Boundary layer height	$-0.19\ (< 10^{-5})$	$-0.24\ (< 10^{-5})$	$0.008\ (10^{0})$
PAHs	$0.79\ (10^{-3})$	$0.76\ (10^{-3})$	$0.59\ (10^{-2})$
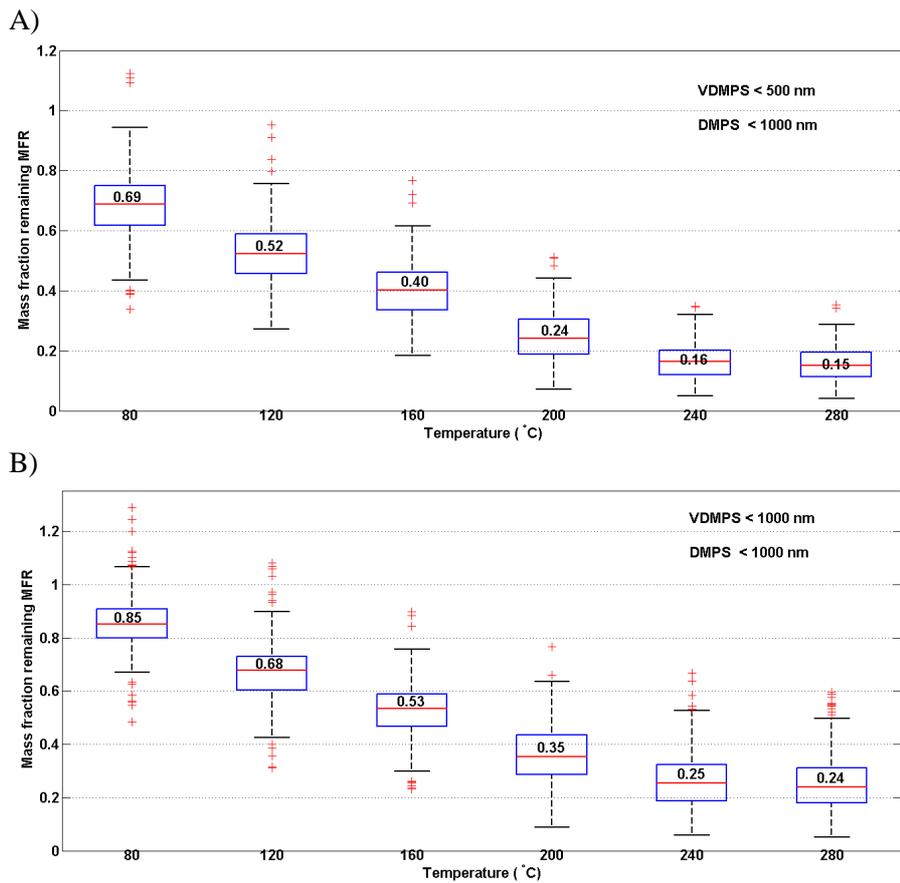
Fig. 2.1 Thermograms describing the aerosol evaporation in different thermodenuder temperatures. Different definitions were used for the MFR: A) MFR (DMPS < 1000 nm and VDMPS < 500 nm) and B) MFR (DMPS < 1000 nm and VDMPS < 1000 nm). Thermograms B and C show the minimum and maximum MFR values, respectively.
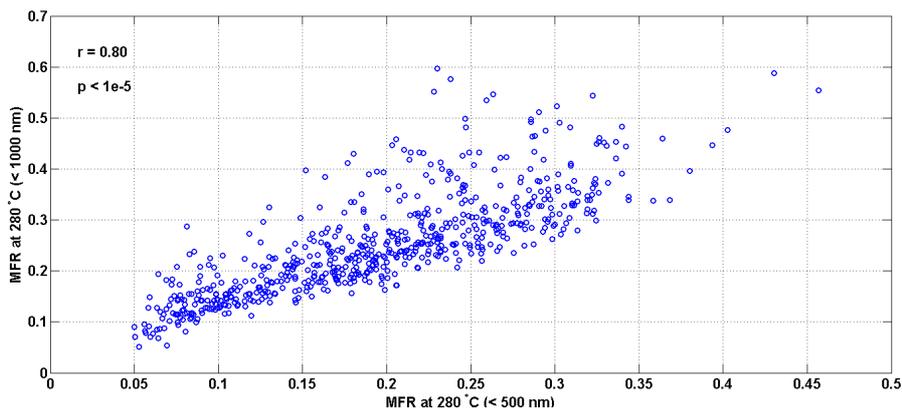

Fig. 2.2 Correlation between MFR (DMPS and VDMPS < 1000 nm) at 280 ℃ and MFR (DMPS and VDMPS < 500 nm) at 280 ℃ that is presented in the manuscript. Correlation coefficient and p-value describing the significance of the correlation are provided in the figure. Correlation is clear and confirms that the size range of 20-500 nm used in the MFR in the manuscript is a representative of the total aerosol evaporation behavior.