

Answers to referee #4 comments: "Long-term volatility measurements of submicron atmospheric aerosol in Hyytiälä, Finland" by S.A.K. Häkkinen et al., 2012.

Answers to Anonymous Referee #4

This paper reports an interesting 2+ years of aerosol composition and the physical property of volatility. It focuses mainly on the non-volatile fraction which it shows nicely but not surprisingly is correlated to and partially explained by BC. There is some attempt to explain the remainder of this non-volatile fraction of PM, much of which occurs in summer, and to link it to organonitrates. This part of the paper is interesting but speculative. It is worth publishing if the authors can clearly distinguish their clear results (i.e. the amount of NV that is BC) from their speculative discussion (about what the rest of it is). I think the former is interesting to the extent that they have been able to quantify the fraction explained by BC, and this result could stand on its own if it is written more clearly.

We agree with you. In the revised manuscript we will put more emphasis on the contribution of BC to the non-volatile (at 280 °C) aerosol residual. We have, for instance, removed all the speculations about the correlations with trace gas concentrations and the MFR(non-BC), inspired by the comments of referee #2. We believe this will make our main conclusion of BC not explaining the material that is left even after heating the aerosol up to 280 °C even stronger.

Referee 2 notes an important mismatch in the size range of the hygroscopicity and the measured NR mass. It's also worth noting the comparison to AMS is comparing the NV to the NR – i.e. what does volatilize at 600 to what didn't at 280 °C. While these are somewhat subtle differences, they are actually quite relevant to the conclusions highlighted here. While I think the work still has merit (i.e. it is not necessarily "flawed" as Referee 2 asserts), I think the authors failed to do a serious job of clearly identifying these mismatches and discussing their impact on the conclusions (and they should be clear in abstract too).

We thank you for your comment and make sure the problems arising from the comparison of data from different instruments are addressed properly in the revised manuscript. Concerning the comparison of VDMPS and DMPS data see answer to referee #2. Concerning the comparison of VDMPS and Aethalometer data see answer to comment #8 by referee #1 and for the comparison of VDMPS and AMS data see answer to comment #1 (Major comments) by referee #3.

OTHER SPECIFIC POINTS TO ADDRESS:

Abstract line 14 – should be "other" not "else"

We will correct that.

Fig 1 – are these the only 2 months that had an AMS at Hyytiälä?

Data presented in Fig. 1 is the data that we used in our analysis concerning aerosol non-volatile (at 280 °C with a residence time of 1.2 s) residual. There was also a third AMS measurement campaign during spring 2009 but because the VDMPS system was not working at that time we could not use this AMS data in our analysis.

Fig 4 – interesting 3-season trend of high BCF in winter.

Long time series makes it possible to capture for example the seasonal pattern of aerosol black carbon fraction. As seen from Fig. 4 the highest values of BCF were observed during winter and fall months. This result is indeed interesting and allows us to speculate the origin of the BC from anthropogenic combustion processes.

Fig 5 – Milagro is misspelled.

We will correct that.

P11204, L 25 - Report exact residence time in the TD.

See answer to comment #5 by referee #1.

P11205, L8 – “It has been observed that almost all submicron aerosol particles...” is an unverifiable statement. Should be tempered, something like, almost all the volatility observations of submicron aerosol particles to date have found they contain...

We will correct that according to your suggestion.

P11206, L4 – Add a statement to explain how this volatility study is different from others conducted at Hyytiälä (e.g. Ehn et al., 2007; Raatikainen et al. 2010).

Our study presents data from two and a half years measurement period and is, therefore, able to capture not only the overall but also the seasonal behavior of the aerosol non-volatile residual. Similar analysis has not been made in a boreal forest environment before. E.g. in Ehn et al. (2007) and Raatikainen et al. (2010) the focus has been in investigating the short-term behavior of the aerosol non-volatile residual by analyzing campaign-based data as well as in case studies. We will add a statement about this to the revised manuscript.

P11207, L25 – Why was it switched to constant temperature operation?

The use of several heating temperatures gives us information about the temperature dependence of aerosol evaporation. However, in order to obtain a full time series of aerosol evaporation it is better to use only one temperature. For investigating the evaporation of aerosol particles at high heating temperatures and studying the “non-volatile residual” more closely constant temperature mode (280 °C) was used during the second half of the VDMPS measurements. We will add mention about this to the revised manuscript.

P11211 – what is size range of aethelometer – i.e. was an 1-micron impactor used?

PM2.5 (2.5-micron) impactor was used (see Sect. 2.2.3).

P11211, L12 – What is the basis for this assumption? Were AMS data or past measurements at the site used to arrive at this figure? What are the consequences of assuming varying particle density for your analyses and conclusions, i.e. how sensitive are your results to the value you use for particle density? If particle density has a seasonal variation then it will influence the seasonal trends reported for MFR.

See answer to comment #2 (Other comments) by referee #3.

P11213, L10 – State heated to 250C

We will add the information about the heating temperature used (280 °C) in Fig. 2.

P11213, L19 – Why? At least state how Ehn et al., (2007) shows this.

Ehn et al. (2007) showed that even almost all nucleation mode particles in Hyytiälä contained material that did not evaporate at 280 °C. Due to this it is probable that the smallest particles cannot be detected in our VDMPS because they evaporate below the detection limit of the system (20 nm). We add a statement about this to the revised manuscript.

P11214, L8 – Despite the increase around 5 or 6/2008 the general trend to me seems to be decreasing MFR at all temperatures to 8 or 9/2008, hard to tell with data gap though.

That is correct. In general the MFR at all six different temperatures behaves the same way.

P11217, L22 – State correlation coefficients here as well as in table 3.

Most of the correlation analysis will be removed due to reasons explained in detail in the answer to the comment of Referee #2..

P11219, L1 – A better section title is ‘Indications of the chemical composition of non-BC MFR.’

We will correct the title to better correspond to its content.

P11222 – reword “explaining factor”, “explaining compound” – what is meant? (The meaning is not clear in English.)

We will reword “explaining factor” and “explaining compound”.

P11222 – polymerization is not the only possible explanation for non-volatile organics.

That is correct. There may be also other chemistry-related processes producing less volatile compounds, e.g. salt formation (Smith et al., 2010). We will note this in the revised manuscript.

P11223 – “aerosol volatility... cannot be explained by any single parameter” – this is poor use of the word “volatility”; here and throughout most of the paper the focus is on the non-volatile fraction, as defined by the 1-sec heating to 280 °C. This constraint should be repeated for clarification to replace the non-specific term “volatility”.

We agree that the word “volatility” has not been used as clearly as it should have been. We will replace “volatility” with more specific phrase “aerosol evaporation at 280 °C in 1.2 s”.