

**Answers to referee #1 comments: "Long-term volatility measurements of submicron atmospheric aerosol in Hyytiälä, Finland" by S.A.K. Häkkinen et al., 2012.**

Answers to Anonymous Referee #1

*The manuscript describes measurements of aerosol volatility in a remote Boreal forest. The measurements are unique in that they continuously span a period of over two years, whereas many other field studies are of much shorter duration. Overall the data are well presented and the analysis is sound. However, the authors need to address several issues in the discussion and interpretation of the results before the manuscript will be suitable for publication.*

*(1) The manuscript makes two conclusions that are never related to one another or resolved. The first is that MFR correlates with PAH concentrations, and thus anthropogenic activity. The second is that MFR correlates with organic nitrates, which I assume must be secondary in nature. How are these two phenomena correlated? Is MFR highest when air masses pass over populated areas (anthropogenic influence) and then have sufficient time (12+ daylight hours) for photochemical processing? This could be inferred from the back-trajectories. One could postulate that the lower-volatility PAHs are picked up in urban areas, stay in the condensed phase because of low volatility, and are joined by anthropogenic nitrate-containing SOA that is formed when NO<sub>x</sub> is high. It is critical to connect these two conclusions, or at the very least note that they are seemingly at odds, rather than to leave them as mere observations.*

In general, the MFR did not show any strong correlation with air mass direction. High MFR values were observed both with polluted and with clean air masses. However, a case study made in fall 2008 AMS campaign showed that high MFR values were observed when air masses were clean, i.e. when particle mass concentration and concentrations of trace gases, such as CO and NO<sub>x</sub>, were low. In that case also the nitrate aerosol mass fraction was high. Unfortunately we have no PAH data available for 2008 to see where the PAHs came to Hyytiälä. It is, however, probable that PAH concentrations were low when also anthropogenic trace gas concentrations were low. All in all, the data we have does not support the assumption that the observed low-volatile nitrate-containing organics are of anthropogenic origin. However, the amount of data is not sufficient to rule out the possible connection between PAHs and the MFR. We will add a mention about this topic to the revised manuscript.

About the effect of aerosol aging on aerosol volatility see also the answer to comment #7 presented by referee #3.

*(2) One important result seems to be the presence of low-volatility OA that potentially contains organic nitrates. This message is buried in the manuscript after much minute detail about what some may consider less-important topics. Authors should consider moving this info to a more prominent location in the manuscript.*

That is correct. One of the main results of this study is that low-volatile OA is a strong candidate in participating in the non-volatile (at 280 °C) aerosol residual. However, this result is highly speculative due to small amount of measurement data available. We make sure that this result will get more emphasis in the revised version of the manuscript.

*(3) The conclusions section should be more focused, not merely a reiteration of earlier portions of the paper. Much of the first few paragraphs of the conclusion are repetitive from earlier in the manuscript.*

We will put more effort to the summary and conclusions section to make it more focused and concise.

*(4) Page 11206-11207 The meaning of DMPS should be introduced with the instrument in section 2.2.1, not as a side note about VDMPS in section 2.2.2.*

We included the meaning of the DMPS (Differential Mobility Particle Sizer) to the section describing the DMPS system we used (Section 2.2.1).

*(5) Page 11207 TD residence time was "around 1 second." It would be preferable to know the centerline residence time at ambient temperature.*

The average residence time in the TD was 1.2 s and the residence time at the centerline was 0.6 s. We will add this to the revised manuscript.

*(6) Section 2.2.5 - Please add PAH filter sampling to Figure 1.*

We will add the PAH filter sampling to Fig. 1 in the revised manuscript.

*(7) Were the DMPS and VDMPS compared at ambient temperature? It seems that the two instruments are different, with different size ranges (20-500nm for VDMPS, 15-1000nm for DMPS). How was this size range discrepancy resolved?*

See answer to the comment of Referee #2.

*(8) Section 3.2 - what fraction of the BC mass is expected to be in particles 500-2500nm? It seems that most of the mass would be in that size fraction. Quantify the effect of this estimate on MFR<sub>non-BC</sub>.*

No measurement data on BC number or mass size distribution is available from Hyytiälä. However, according to literature (e.g. Hitzenberger and Tohno, 2001; Schwarz et al., 2006; Shiraiwa et al., 2007; McMeeking et al., 2010) only a negligible amount of BC particles is observed in the size range of > 500 nm, even close to urban areas. However, the contribution of BC mass in the size range of > 500 nm is non-negligible. By using the modal parameters presented by Hitzenberger and Tohno (2001) for mass, it can be estimated that the BC mass contribution in the size range of > 500 nm is about 15-20 % in urban areas. This can be taken as an upper limit of BC mass contribution to particles larger than 500 nm in a background station SMEAR II in Hyytiälä. The absolute maximum error introduced to the MFR (non-BC) would be around 30 % if 20 % of the BC mass would be in particles larger than 500 nm in diameter. Therefore, the BCF we used in our study presents the maximum value for the BC mass fraction in particles < 500 nm and thus MFR(non-BC) is the absolute minimum value. We will add this discussion to the revised manuscript.

*(9) Page 11214, Lines 5-6 "During winter and fall periods, the temporal variation of the MFR values was relatively similar independent on the TD temperature." What exactly does this mean? Please clarify.*

It means that the observed temporal pattern of the MFR values was the same independent on the heating temperature. High MFR values at low heating temperature corresponded high MFR values at high heating temperatures. This will be clarified in the revised manuscript.

*(10) Page 11214, Lines 6-8. "During the spring and summer months, however, the MFRs below 200 C seemed to show an increasing trend while the MFRs at higher temperatures were decreasing." I never see*

*the "low temperature" MFR moving a different direction than the "high temperature" MFR. In the fall/winter the higher temperature MFR level off while the low temperature MFR slightly increase. Also from winter into spring, the higher MFR seem to have a bigger downward slope than the lower temperatures.*

We agree with your comment on the fact that from winter to spring MFR seems to have a bigger downward slope at higher temperatures. By saying "During the spring and summer months, however, the MFRs below 200 °C seemed to show an increasing trend while the MFRs at higher temperatures were decreasing." we mean somewhat the same thing. During April/May 2008 and March 2009 a difference between the MFR of higher temperatures and the MFR of lower temperatures as a function of time can be seen. At higher temperatures (> 200 °C) the MFR decreases continuously, whereas at the lower temperatures this is not the case. We will make this statement clearer in the revised manuscript.

*(11) Figure 4 - are these raw MFR or MFR<sub>non-BC</sub>?*

They are raw MFR values. We will make it clear to the reader.

*(12) Page 11214, Line 20. "Residence times and aerosol type varied from study to study" This is important, because residence time matters in the TD. Make this point more strongly.*

We agree. We will put more emphasis to it.

*(13) Table 1 can probably go into the supporting info. I don't think it's critical to interpreting the TD results.*

We will make the change according to your suggestion (Appendix A in the revised manuscript).

*(14) Figure 5: it's hard to distinguish between black and grey points.*

We will modify Fig. 5 accordingly.

*(15) Page 11215, Lines 21-26 - Does the calculation following Riipinen's method include a BC fraction? Or is this strictly for the measured MFR represented by a single component organic particle?*

The method presented by Riipinen et al. (2010) is for the evaporation of semi-volatile organics in a TD and thus, it does not include the effect of non-volatile compounds such as BC. However, BC aerosol fraction can be easily included in the model calculations. Running the model as a two component system did not affect the results strongly. Compared to the organic single component calculation adding BC to the model increased the enthalpy of the organic aerosol fraction from 60 kJ mol<sup>-1</sup> to 64 kJ mol<sup>-1</sup>. We will add these results to the revised manuscript.

*(16) The caption to Figure 5 states that the line assumes that "all nonvolatile aerosol mass is BC". This implies that some of the OA is "nonvolatile". I disagree with this in an absolute sense. ALL OA is semivolatile. It is apparently nonvolatile in the context of your TD, residence time, etc.*

We agree. In the text we have misleadingly used the word non-volatile without explaining carefully what we mean. By non-volatile we mean material that is not evaporated in our TD at 280 °C in an average residence time of 1.2 seconds. We will make this clear in the revised manuscript.

*(17) I recommend against circling the  $r^2$  in figure 6.*

We will modify Figure 6 according to your suggestion.

(18) Page 11216, Lines 12-14 *"although specifically in summer the black carbon concentrations were often of similar magnitude than the concentrations of the non-volatile material."* Again there is confusing interchange between BC and nonvolatile material. BC is truly nonvolatile. I suggest changing the wording and calling the non-evaporating, non-BC fraction of the aerosol something else. Perhaps *"non-evaporating"*.

We understand your point. We will make sure that what we mean by "non-volatile" residual is clear in the revised manuscript.

(19) Page 11216, last line. *"non-volatile particle mass fraction"* requires some thought to deconvolute. It probably gets boring to keep writing MFR, but it is easier for the reader to interpret. Also, it implies that everything that does not evaporate in the TD is nonvolatile.

We will use MFR and MFR(non-BC) consistently throughout the text.

(20) Page 11218, lines 3-4 *"It is possible that some of the PAHs having low saturation vapor pressures, around  $1e-7$  Pa."* The mass fractions of the PAH (tot PAH always < 1%) are not sufficient to drive significant differences in MFR. Also, some of these PAH have  $C^* > 1$   $\mu\text{g}/\text{m}^3$ . The PAH seem useful as an indicator of anthropogenic influence, but are not a major component of OA or the MFR.

That is correct. The mass concentrations of PAHs are too low to have a significant, if any, contribution to the MFR(non-BC). However, as you pointed out the observed correlation should be rather taken as a sign of anthropogenic influence. We will emphasize this in the revised manuscript.

(21) Page 11218, middle paragraph - I suggest moving this up, immediately after the other paragraph discussing ambient temperature.

See answer to your comment #22.

(22) In general section 4.4 could benefit from some reorganization. There is a sometimes confusing mixture of variables (temperature, trace gases, etc) and seasonality. I suggest the authors try to be more systematic in the discussion. I.e., focus on seasons first, then variables.

We will revise the whole section 4.4. Most of the correlation analysis will be removed due to reasons explained in detail in the answer to the comment of Referee #2.

(23) Perhaps switch Figures 7 and 8. Figure 7 is introduced first, but only briefly. The major discussion of it is after the major discussion of Figure 8.

We will remove the introduction of Figure 7 from the text and therefore switch Figures 7 and 8.

(24) Figure 10 is not discussed enough to make it essential to the manuscript. I recommend moving this to supporting information. In general, the last paragraph of section 4.5 seems superfluous and/or misplaced. It seems to show redundant info as Figure 9 - high correlation of aerosol nitrate with MFR<sub>non-BC</sub>.

We agree. We will remove Fig. 10 to the supporting information (Appendix A). We will also revise section 4.5.

References:

Hitzenberger, R., and Tohno S.: Comparison of black carbon (BC) aerosols in two urban areas - concentrations and size distributions, *Atmos. Env.*, 35, 2153-2167, 2001.

McMeeking, G. R., Hamburger, T., Liu, D., Flynn, M., Morgan, W. T., Northway, M., Highwood, E. J., Krejci, R., Allan, J. D., Minikin, A., and Coe, H.: Black carbon measurements in the boundary layer over western and northern Europe, *Atmos. Chem. Phys.*, 10, 9393–9414, doi: 10.5194/acp-10-9393-2010, 2010.

Schwarz, J. P., Gao, R. S., Fahey, D. W., Thomson, D. S., Watts, L. A., Wilson, J. C., Reeves, J. M., Baumgardner, D. G., Kok, G. L., Chung, S. H., Schluz, M., Hendricks, J., Lauer, A., Kärcher, B., Slowik, J. G., Rosenlof, K. H., Thompson, T. L., Langford, A. O., Lowenstein, M., and Aikin, K. C.: Single-particle measurements of midlatitude black carbon and light-scattering aerosols from the boundary layer to the lower stratosphere, *J. Geophys. Res.*, 111, D16207, doi:10.1029/2006JD007076, 2006.

Shiraiwa, M., Y. Kondo, N. Moteki, N. Takegawa, Y. Miyazaki, and Blake, D. R.: Evolution of mixing state of black carbon in polluted air from Tokyo, *Geophys. Res. Lett.*, 34, L16803, doi:10.1029/2007GL029819, 2007.