**Atmospheric
Measurement
Techniques
Discussions**

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Interactive comment on "Optical properties of a heated aerosol in an urban atmosphere: a case study" *by* J. Backman et al.

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First of all we want to thank the Referee for the constructive feedback and knowledge to make this article scientifically more accurate and solidly founded.

Answers to the general comments

Comment: After reading the Abstract and the Introduction, the title of the paper "Optical properties of a heated aerosol in an urban atmosphere: a case study" doesn't seem to carry the main message of the manuscript. For instance, the sentence of the abstract "Light absorption measurements most commonly rely on filter-based measurement tech... are disturbed by light scattering constituents in the aerosol deposited

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on the filters, and the description in the introduction "the aim was to show a proof-of –concept that the performance of the filter –based methods can be..." give the impression that you are trying to focus to improve the light absorption measurements by filter based techniques. It would be good to synchronize the main message in the Title, Abstract, Introduction, as well as in other parts of the paper.

Answer: As filter-based methods are influenced by light scattering species deposited in the filter matrix their effect can be made smaller by removing them before they enter the filter. In sub-micron particles the scattering aerosol constituents are mainly volatile at temperatures close to 300 °C so we have minimized the amount of scattering aerosol species by heating the sample air and so the uncertainties associated with the scattering correction in the algorithms generally in use.

The aim was to study whether the performance of the filter-based methods for measuring light absorption by aerosols can be improved with the aid of volatilization. Different mixing states of soot due to volatile species increase the uncertainty of estimation of BC concentration from absorption measurements because mixing states changes light absorption. In principle this uncertainty can also be minimized by volatilisation and we wanted to study how.

These were the goals of the study. As both referees kindly pointed out this message is not entirely clear throughout the paper. To clarify, the title of the paper was changed from "Optical properties of a heated aerosol in an urban atmosphere: a case study" to "Impacts of volatilisation on light scattering and filter-based absorption measurements: a case study" along with the message in the Title, Abstract and Introduction along with other parts of the paper to match the scope of the manuscript.

Comment: If the main message of the manuscript was intended to improve the filter based measurements of aerosol light absorption, then more discussion and analysis pertaining to the interaction of the aerosol with the filter media would justify the scope of the manuscript. Sheridan et al. reported that at higher absorption (at lower single

scattering albedo) the aerosol light absorption measurements by PSAP deviates more from the reference absorption due to the inadequate filter loading correction [Sheridan et al., 2005]. This situation should be more pronounced in this work due to the evaporation of the volatile aerosols at the elevated temperatures, and so the reduced amount of the scattering aerosols on the filter matrix should also have an effect on both Bond and Virkkula algorithms used in this study.

Answer: The last comment above is true, the reduced amount of scattering aerosols really has effect on both the Bond and Virkkula algorithms. In both of them there is a subtraction of scattering coefficients and the subtrahend gets significantly smaller, as well as the uncertainty associated with it. For the Virkkula algorithm the additional effect is due to the decreasing single-scattering albedo. Since after heating we had a dark aerosol (low single-scattering albedo) the influence of the correction function which compensates for scattering and filter loading gave different results yielding significantly different MAC for soot. As was shown by Sheridan et al., 2005 and Virkkula et al. 2005 the more frequently used PSAP correction function of Bond et al. (1999) deviated more from the reference absorption for a dark aerosol the heavier the filter loading.

Comment: Discussion should have been focused on the appropriate temperature at which the aerosol should be heated to improve the light absorption measurements by using the filter method.

Answer: We have discussed on the appropriate temperature mainly by referring to previously published data on volatility. To really focus on the appropriate temperature we should have made both internal and external mixtures of soot and different scattering species. We only tested ammonium sulfate and sodium chloride in the laboratory to see that our thermodenuder actually volatilizes known species at temperatures presented by other groups as well. With the oven and the setup we used we had to make do with a residence time of 1.0 second and a temperature of 300 °C. Volatility is a function of both temperature and residence time. By heating the aerosol to 280 °C for 1.0 seconds we got a MAC of 9.6 m^2g^{-1} at 545 nm when using the Bond et al. 1999

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algorithm without compensating for penetration depth. This compares good with the MAC of m^2g^{-1} at 565 nm measured by Miyazaki et al., 2008 after heating the aerosol to 400 °C which also estimated some influence of pyrolysed organic carbon.

Comment: This method is highly sensitive to how deeply the particles were deposited in the filter. For an example, see Arnott et al., 2005.

Answer: This is true and a very good comment. We did not take this into account in the first version of the manuscript. By evaporating volatile constituents from the aerosol phase the particles shrink in size. Since filter penetration among other things is a function of size (VanOsdell et al., 1990). Filter-based methods for measuring absorption are, as was kindly pointed out by the referee, sensitive to how deeply the particles penetrate the filter until they are deposited (e.g., Arnott et al., 2005; Nakayama et al. 2010). Thus, by heating and shifting the mode of the size distribution towards smaller sizes we alter the penetration of the particles and therefore increase the instruments response to light absorbing particles deposited on the filter. In the revised version a new analysis will be done using the parameterization of Nakayama et al.(2010). This was done using size distribution data yielded significantly lower MAC values 10.1 and 7.2 m^2g^{-1} for the Virkkula and Bond algorithms respectively. On average the light absorption values were lower by a factor of 0.7 with the Nakayama parameterization than without it.

Comment: The hypothesis in both the Abstract and Introduction "the filter based measurements are disturbed by light scattering constituents" doesn't seem to be supported by further example; the nature of the filter used in aethalometer, the PSAP and phenomenon of multiple scattering in the filter matrix, and the types of aerosol that would be mostly effected by the filter should be described to support the hypothesis.

Answer: We don't quite understand this comment. It is not really a hypothesis, it is well known that the filter-based measurements show absorption even if there is only scattering aerosol present. How much this "apparent absorption" is has been discussed in

other papers and it has been shown that it is not a constant factor of the scattering that could be subtracted – even though it is used frequently so. This is what we mean when we write "... are disturbed by light scattering constituents...". We have rephrased the sentence and not used the word disturbed.

Comment: The elevated temperature definitely effects the morphology and fractal state of the black carbon in comparison to its ambient state there by changing the optical properties. This should be included in the discussion of the manuscript. For more discussions pertaining to the surface modifications of hydrophobic and hydrophilic soot on optical coefficient see Mikhailov et al., 2006.

Answer: The change in morphology when exposed to higher humidity has been discussed by several authors. Mikhailov et al., 2006 showed that when hydrophilic (HLS) soot particles act as condensation nuclei their initial fractal structure collapses to form spherical soot cores and that the absorption cross section grew with a non-absorbing liquid shell around the particles. We did not find any papers on the morphology of atmospherically aged soot exposed to a thermodenuder and since we did not take microscopic pictures of the residual particles we can only make educated guesses. Slowik et al., 2007 showed that the collapse of the fractal state is a function of coating thickness and some rearrangement towards a fractal state after thermodenuding. The experiment by Slowik et al., 2007 was conducted with oleic acid and a thermodenuder operating at 200 °C. However, the effect on cloud processed atmospheric aerosol consisting of a vast variety of different volatile inorganic and organic species is unknown to us. The soot that is in the core of internally mixed particles is probably already in a collapsed state. When the outer shells are volatilized by heating the collapsed soot core is assumed to remain collapsed. We also have to assume fractal like soot to be unchanged in the thermodenuder. These assumptions will be addressed in the final manuscript along with the influence of broad side enhancement by the alignment of the deposited fractal like particles.

Comment: At the same time the heating of the aerosol might lose its coating and mixing

state, so we also might lose this important information about the ambient aerosol.

Answer: This is true. After heating we most probably just have externally mixed soot particles. As we replied also to Referee 2, volatilization will lead to bias, actually under-estimation of absorption because the true absorption of light by particles is larger for internally mixed than for externally mixed particles. By volatilizing the material surrounding an absorbing core the true absorption decreases. For externally mixed absorbing and scattering aerosol this would not happen. If there were ideal, artifact-free absorption measurements the absorption coefficients measured from heated and non-heated sample lines would tell whether the absorbing and scattering particles are internally or externally mixed.

But still, we may expect to get more accurate estimation of BC mass concentration from absorption measurements after volatilization since the remaining absorption should be by externally mixed soot alone without the uncertainty associated with scattering species.

Comment: The reported mass absorption coefficient (MAC) in this manuscript; 13.5 m^2g^{-1}, calculated by heating the aerosol using PSAP seems quite higher at 545 nm than the published value. For example Fuller et al. suggested MAC less than 7 m^2g^{-1} for diesel soot at 550 nm [Fuller et al., 1999], and Bond and Bergstrom have proposed a value 7.5 m^2g^{-1} for pure soot carbon particles [Bond and Bergstrom, 2006]. As mentioned in the paper at an elevated temperature of 280 °C the only aerosol remaining in the filter is dominantly of black carbon, so in this condition the calculated MAC shouldn't be so high because the residual aerosol is free of any kind of coating and internal and external mixing.

Answer: When the discussion paper was submitted we were not aware of the parameterisation of Nakayama et al., 2010 for the size dependent correction for penetration depth in the filters.

For the revised manuscript we have corrected for the size dependency of the measured

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size distribution, using the Nakayama method.It lowered the MAC's from 13.5 to 10.1 m^2g^{-1} and 9.6 to 7.2 m^2g^{-1} for the Virkkula and Bond algorithms respectively, at λ = 545 nm. These are more in agreement with what was suggested by Fuller et al., 1999 and Bond and Bergström 2006.

Answers to the specific comments

Comment: (1) Do you mean due to their size or their chemical composition? Further, this sentence would be more appropriate if you were selecting the size of aerosol in that range during your measurement period.

Answer: We meant chemical composition. The sentence was changed to "Most light scattering constituents in a sub-micron aerosol are volatile by their nature due to their chemical composition and can be volatilized by heating the sample air."

Due to the PM10 inlet to the campaign instruments they were not only measuring sub-micron particles. In these sub-micron particles we expected the light scattering species to be completely or partly evaporated at 280 °C. In the super-micron aerosol we would expect to find crustal material and sea-salt which also scatter light which aren't volatile. To assess this influence Aerodynamic Particle Sizer (APS) and DMPS data the fraction of scattering by PM1 particles to PM10 was calculated with Mie modelling. This issue will be addressed in the revised manuscript.

Comment: (2) Why is the MAC to different for the same wavelength? I don't think these values are themselves consistent. Why do you choose the first one to report in the abstract? The MAC 13.5 m^2g^{-1} seems too high at this wavelength, so you must need to say something about why it is so high and why you are getting differing values by applying Virkkula and Bond et al algorithm.

Answer: As was shown by Virkkula et al. the Bond et al., 1999 correction underestimates absorption at low single-scattering albedos yielding a lower MAC. Since the single-scattering albedo of the residual aerosol was dark we chose an algorithm which

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takes the single-scattering albedo of the aerosol into account. However, in the revised version abstract we will present the MAC that will be calculated also according to the Nakayama et al. 2010 correction with both algorithms.

Comment: (3) You should explain the abbreviation of SMEAR III (Page 1583, line 10), and OC1, OC2, OC3, OC4 (page 1595, line 9)

Answer: These abbreviations will be explained in the text.

Comment: (4) "All the notations used in equations (6), (7), and (8) should also be defined in the text."

Answer: All notations will be defined in the text.

Comment: (5) The sentence "suggesting that noisy . . .periods may have been due to near-by soot sources" on page 1594, line 21 is quite confusing. Were the "soot sources" presented for only one particular time of the measurements? If there were soot sources nearby, they should make the signal more robust rather than making it noise.

Answer: As you kindly pointed out this needs further explanation since strong soot sources should make the signal more robust. The SMEAR III station is located near the beginning of a high-way so the local soot sources referred to are vehicles standing in traffic lights. The highway sector and wind direction were plotted and added as a supplement picture to the discussion. This issue was also clarified in the text page 1595 line 21 "... suggesting that the noisy $\sigma_{AP,PSAP}$ periods may have been due to near-by soot sources such as heavy traffic and vehicles."

Comment: (6) The magnitude of observed single-scattering albedo have been reported as 0.5 on page 1595, line 30 and 0.4 on page 1598, line 25. Were both descriptions intended for maximum SSA observed after midnight on April 13?

Answer: No, the SSA of 0.5 discussed on page 1595 line 30 is in the context of constant oven temperature and an event were we observed a jump in SSA from 0.3 to 0.5 after

midnight on April 13. The SSA discussed on page 1598 line 25 is in the context of the variable temperature scans and how low-volatile organics may affect the calculated values during the 14-15 April.

Comment: The explanation for this increased SSA (chemically different aerosol entering the oven in the first instance and organic carbon in the second instance) is not convincing. The mid visible wavelength should not be so much affected by organic carbon on the other hand to have organic aerosol there must be some noticeable different activity going on like bio-mass burning. The mid visible wavelength should not be so much affected by organic carbon on the other hand to have organic aerosol there must be some noticeable different activity going on like bio-mass burning.

Answer: Organic carbon also scatters well in the visible wavelengths. So if there is some OC that does not evaporate at 280°C, it will scatter light and SSA will be higher. However, we will now make a more moderate statement. The reason is that at the same time of the increase of SSA the scattering coefficient increased from $\approx$20 Mm^{-1} to $\approx$100 Mm^{-1} so the increased SSA might also be an indication of that the residence time was not enough to volatilize all compounds. On the other hand, during the temperature scanning period of April 14-15 the non-heated scattering coefficient was also $\approx$100 Mm^{-1}, even slightly higher than on April 13, but SSA was clearly lower (0.2 - 0.4) than on April 13. So these suggest that the reason actually is a chemically different aerosol. We also did a trajectory analysis using HYSPLIT. On April 13 air had flown from over western Russia and on April 14-15 from over the Baltic States. In these the various aerosol source types are different so it also supports the statement that the aerosol was chemically different. We will add an explanation to the text but not plot any trajectories; it would increase the paper length unnecessarily.

Answers to comments on figures

Comment: Figure (2) You should label upper panel and lower panel as Figure 2 (a), and 2(b). The error bars in upper panel are not consistent in length; the error bars

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are higher at the beginning and decreasing and increasing. Is there any particular reason for this, because in the lower panel it is decreasing continuously with the particle concentration?

Answer: The figures panels were labeled according to the suggestion. The data was collected by scanning different temperatures and measuring the size distribution. The error bars are the standard deviation of the calculated values at a certain temperature. Since the values are normalized they tend to decrease with the measured concentration. This specification was added to the figure caption.

Comment: Figure (3) This figure seems much too busy

Answer: The figure was split in two. The X-axes were labeled "Dates in 2009" and font size increased. The figure was split in two with OC/EC, scattering and absorption coefficients in one figure and NVFR and single-scattering albedo in one figure.

Comment: Figure (3) I don't see any point in including data of variable temperature in this plot

Answer: The variable temperature data was plotted into the same picture because it was the first weekday after the national holiday with elevated levels of local emissions. This is not obvious if they are plotted in different pictures. We would kindly ask to keep the variable temperature data plotted in the same picture.

Comment: Figure (7) Give some explanations on how you calculated the error bar of the single scattering albedo and how does it propagate from both absorption and scattering measurements?

Answer: The single-scattering albedo and the non-volatile volume fraction remaining were calculated from the temperature scans (two measurements per temperature) shown in Fig. 5 in the discussion paper. Absorption and scattering data were averaged over the duration of the DMPS scans which were used to calculate the single-scattering albedo. The error bars were calculated using the standard deviation of the results from

these scans.

REFERENCES not found in the discussion paper

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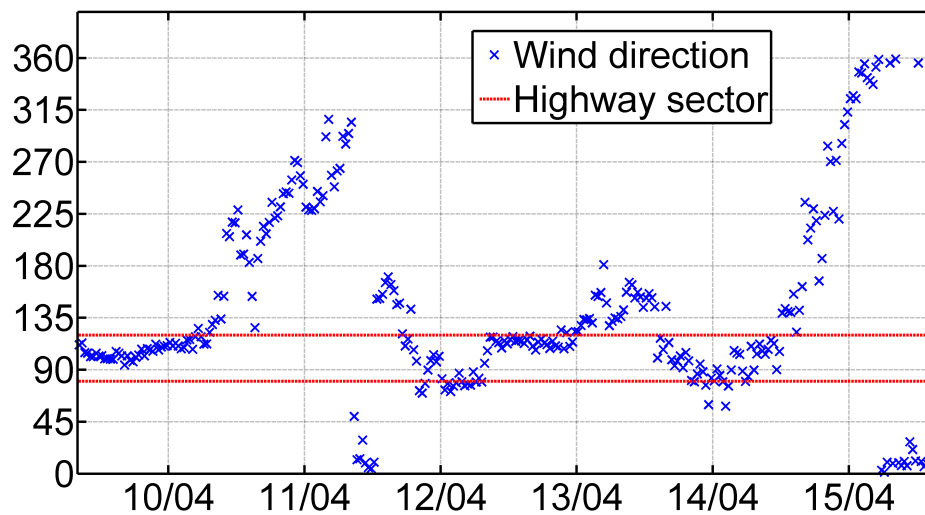Printer-friendly Version

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Fig. 1. Highway sector for the SMEAR III station and wind directions during the campaign