amt-2016-285-RC1-supplement

Review of

« The filter loading effect by ambient aerosols in filter absorption photometers depends on the mixing state of the sampled particles », by L. Drinovec et al.

Main comments:
-The filter absorption photometers suffer from several artifacts and the filter loading effect is only one of them. The other artifacts and principally the multiple scattering effect that have the greatest impact on the calibration of the instruments have at least to be mentioned in the abstract and described in the introduction.

ResponseRC1.1: We have modified the text accordingly:
Abstract (lines 31-33): "Black carbon measurements are usually conducted with absorption filter photometers, which are prone to several artefacts including the filter-loading effect – a saturation of the instrumental response due to the accumulation of the sample in the filter matrix.".
Introduction (lines 69-73): "The measurements ~~are~~, however, ~~prone to several artefacts including~~ depend on the multiple light scattering within the filter, and are prone to several artefacts including the filter loading effect and particle scattering (Lack et al., 2014). Herein we focus on the filter-loading effect (FLE), a saturation of the instrumental response due to the accumulation of the sample in the filter matrix (Bond et al., 1999; Weingartner et al., 2003; Moosmüller et al., 2009)."

Moreover, if a comparison with a non-filter based instrument or at least a MAAP during the Ljubljana campaign with drying and denuder, it would allow to gain extremely useful information on the dependence of the multiple scattering effect on the coating of the particles.

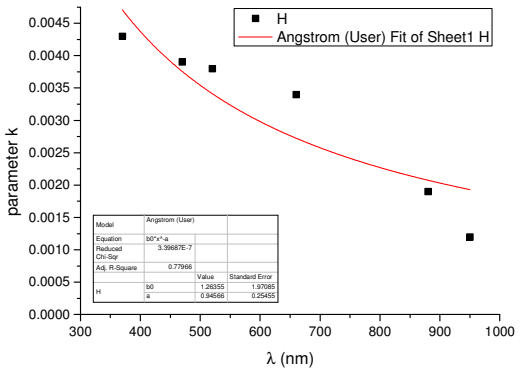
ResponseRC1.2: MAAP was not available for the selected campaign. We agree that it would be advantageous to have an artefact free aerosol absorption method.

- to my knowledge, there is no dependency of the AAE to the aerosol size (or size distribution). I think that there is a mismatch in the paper between the AAE and the scattering Angström exponent that really depends on the aerosol size (for ex P. 12 lines 324-325, conclusion lines 528-530).

ResponseRC1.3: The influence of particle, core and shell size can strongly influence *AAE* as pointed out by the rewiever #2 who proposed references: Gyawali et al., ACP 9, 8007–8015 (2009); Lack & Cappa, ACP 10, 4207–4220 (2010). For fresh winter emissions, we assumed that aerosols are an external mixture of black carbon particles of the size between 30 - 160 nm and tar balls. For the selected particle sizes we expect *AAE* close to 1. We explain the increase of the loading parameter k_6 with *AAE* (Figure 5) with the increase of the BC particle size. The dependence of *AAE* on the black carbon particle size is in our case circumstantial. The comparison of the loading parameter k_6 for different BC particle sizes with *AAE* values close to one shows an increase in k_6 when size distribution moves to larger diameters (Figure 6). Ambient *BC* from biomass burning features larger particle sizes than BC from fossil fuel combustion and is co-emitted with brown carbon. The increase in *AAE* is caused by additional absorption of brown carbon in tar balls. We therefore associate the increase in k_6 with *AAE* to be due to BC particle size.

- Instead of using k6 for a large part of your study, wouldn't it be better to calculated the k Angström exponent that is the wavelength dependence of k ? Do you have an explanation why the size distribution and the coating have such a large impact on the wavelength dependence of k ?

ResponseRC1.4: parameter *k* does not follow the power law:



Virkkula et al (2015) have shown that the value of k_6 and the wavelength dependence of k (as parametrized by a linear slope a_k) are homologous (please see also the ResponseRC1.25).

We believe that interplay between the depth distribution of particles and light intensity inside the filter is responsible for the filter loading effect. More research is needed to determine the mechanism of the filter loading effect, including laboratory experiments interpreted with a very intricate light transport model similar to Mueller et al. (2014).

- Fig. 8: If I do agree with the linear correlation between k6 and CF for both summer campaigns, the winter campaigns both in Paris and in Payerne cannot be fitted by a lineal and the decrease of k6 with CF is not clear. Is there difference in the chemistry of the coating as a function of temperature explaining this difference? Sentence lines 384 should be consequently changed as well as p. 16 lines 393-395.

ResponseRC1.5: Coating factor (*CF*) describes the material available for coating. During summer, most of the organic material is secondary (Freutel et al. 2013) and it condenses on the existing particles in the atmosphere, resulting in coated BC particles. For biomass burning emissions, the particles are externally mixed (Healy et al., 2013) - having high *CF* but no coating. The relationship between *CF* and the mobility diameter peak position (Figure S2) shows an evident increase of the particle size with increasing coating factor, which indicates that aerosols are internally mixed. During winter, there is an increase of particle size with $CF < 12$; for bigger coating factors, the particle size does not increase – this is expected for externally mixed aerosols. We believe this explains the dependence between *CF* and k_6. As reported in Table 4, the fitted slopes are negative for Paris and Payerne in winter and in summer. The dependence, however, deviates from the linear one in Paris in winter.

We have modified and added to the text describing Fig. 8 (lines 418-433):
"We have observed a ~~decrease~~ change of k_6 with increasing coating factor for all four campaigns. The decrease is of different magnitude and shape for summer and winter. The decrease is larger in summer than in winter. In summer in Paris and in Payerne in both seasons, the relationship is linear, while the shape is more complex in Paris in winter.

The results are most pronounced for the Paris summer campaign with the largest absolute slope of the linear regression line. In Payerne in summer, the slope is slightly lower. In summer, k_6 reaches zero at coating factor values of approximately 30 for both locations (Table 4). These results show that during summer the coating material causes a reduction of the filter loading effect. In Paris, *CF* is much larger compared to Payerne. Because most of the non-refractory material in Paris during the summer is of secondary origin (Freutel et al. 2013), it is possible to form internally mixed aerosols in the atmosphere. The correlation of particle size with coating factor in Paris supports this assertion (Figure S2).

The fitted slope obtained for the Paris winter campaign is lower compared to summer and k_6 reaches zero at CF=57, with the dependence being more complicated than the linear one observed in summer. There is almost no ~~correlation~~ decrease of~~between~~ k_6 ~~and~~with increasing *CF* during winter in Payerne."

Minor comments:
- It is not usual to have a complete sentence as a title, but this is ok for me
- A brief paragraph with a very succinct description of the study should be added at the end of the

introduction.

ResponseRC1.6: A brief description and the rationale of the measurement campaigns were included and the introduction now finishes with the following paragraph (lines 105-116):
"We conducted field campaigns in contrasted environments to determine the influence of sources, particle age and coating on the magnitude of the FLE. ~~For clarity a brief description of the camaigns and the rationele is presented here. First w~~We show that the FLE during the one yearlong campaign in Paris ~~showing~~features distinct winter and summer patterns~~, respectively~~. Winter dependence of the FLE is discussed in the ~~view~~context of presented ~~ of Reno~~laboratory experiments with BC of different particle size. Winter and summer intensive campaigns in Paris and Payerne allowed us to determine ~~a~~the coating factor, which represents the relative contribution of the material available for coating. The FLE behavior during summer reveals an~~possible~~ influence of particle coating on the FLE. As ~~the~~ particles get coated by secondary material ~~as part of~~during atmospheric ageing, we ~~followed~~show, using ~~backtrajectories~~backtrajectory analysis, that~~to assign~~ the FLE depends on the particle age ~~to the FLE~~. The ~~final~~ambient campaign ~~was performed~~ in Ljubljana ~~where~~quantifies the increase of the loading effect when ~~the consequences of~~ the particle coating is removed ~~removal were investigated~~. "

- P, 4 line 103: I think that the present should be used.

ResponseRC1.7: Text is changed to (lines 122-123)" *BC* and absorption coefficients are ~~was~~ characterized with the dual-spot Aethalometer (Magee Scientific Aethalometer model AE33) with real-time loading compensation (Drinovec et al., 2015). "

- P. 4 lines 105 and 121: the flow is first said to be different for each spots and then (121) a unique flow rate of 5 lpm is given.

ResponseRC1.8: the sentence has been changed to (lines 139-140): "Instruments were run at 5 LPM~~lpm~~ total sample flow and 1 minute time resolution."

- P. 5 line 148: above sea level == a.s.l.

ResponseRC1.9: "above sea level" was changed to a.s.l. (lines 169-170): "The observatory sits on a plateau, about 160 m ~~above sea level~~a.s.l., in a semi-urban environment being divided between agricultural fields, wooded areas, housing and industrial developments."

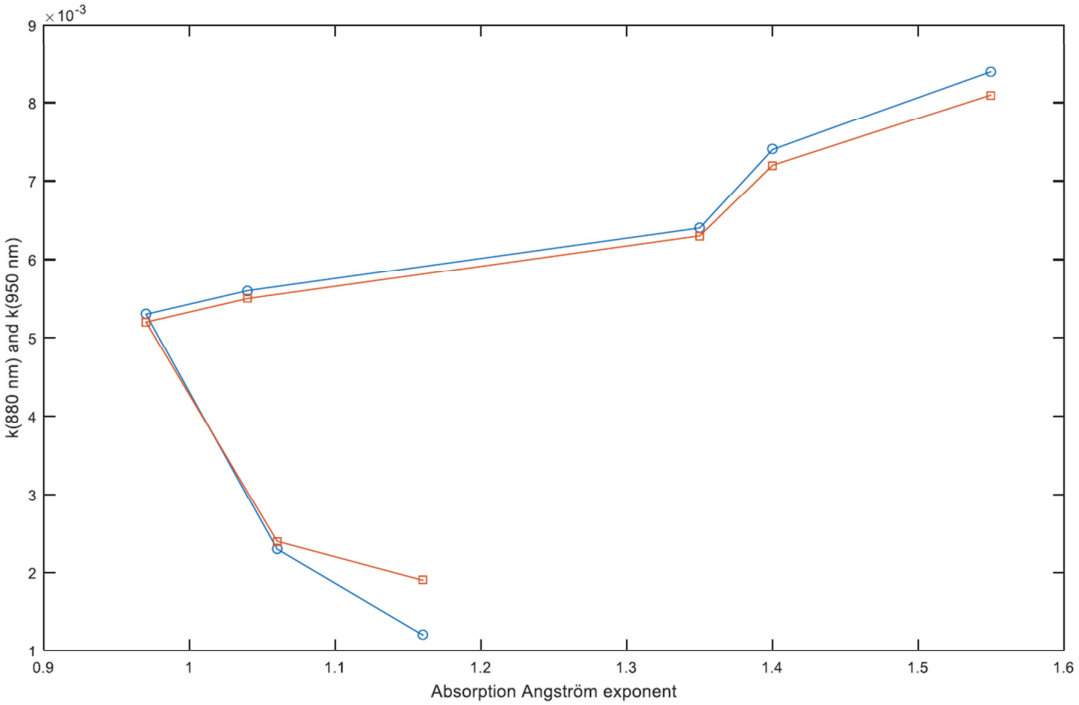
- P. 6 line 203: why did you chose 500 a.g.l. for the trajectory end and not the surface ? Is it possible that the stable boundary layer during the night is lower than 500 m a.g.l. ?

ResponseRC1.10: We agree that it is possible that the stable boundary layer height (BLH) might be < 500 m during the night. Theoretically, BLH should be taken into account for each data point to ensure that the corresponding backtrajectory ends within the boundary layer, but this would require measurements that were unfortunately not available at both sites. We used 500 m a.g.l. height mainly because it is a fairly good average of BLH, due to the coarse resolution of the topography in HYSPLIT, and also for consistency compared to previous studies (Bressi et al., 2014, Waked et al., 2014).

- - Fig. 1 & 4: it seems that there is a change in the wavelength dependence at 660 nm. Do you have an explanation for this phenomena found at least in 4 of the fingerprints of Fig. 1 ?

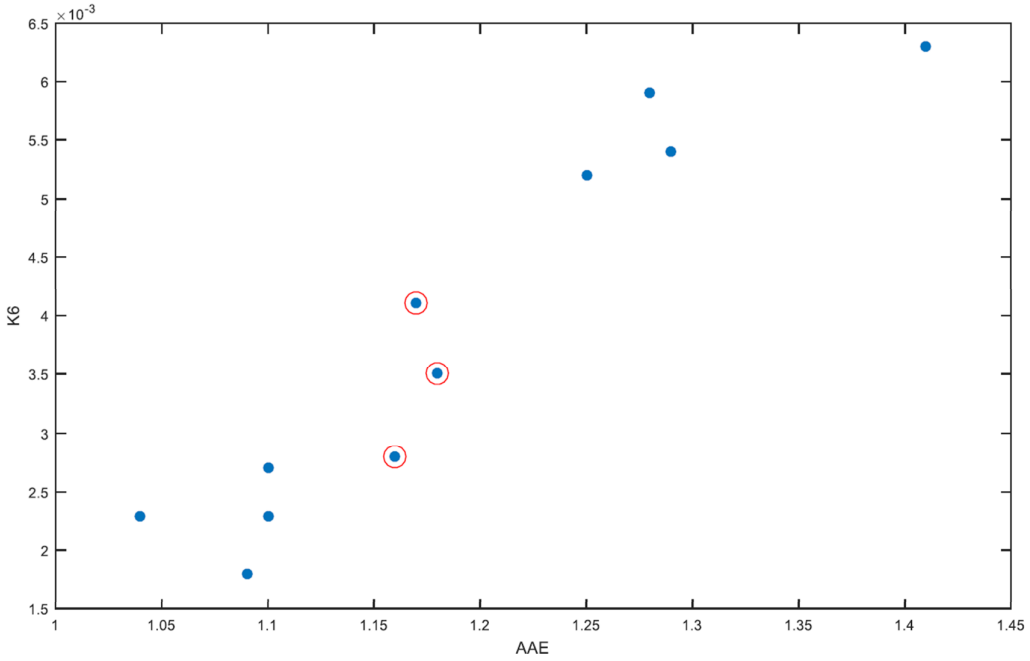
ResponseRC1.11: This feature is not common to all measurements and it may be site or aerosol composition specific – a change has previously been observed in Hyytiälä in summer, but not in winter (Virkkula et al., 2007).

- P. 98 line 240: " Occurrence of higher k values appears to be linked to the latter parameter" : do you speak of the k values at 880 or 950 nm that are linked to the absorption Angström exponent ? This seems to be right for the laboratory and winter campaign data, but not for the summer campaign (see also next figure).



ResponseRC1.12: The ”latter parameter” corresponds to the Ångström exponent. Higher k values (in the infrared) are linked to higher Ångström exponents. We obtain high values of k_6 for »K-puszta – winter«, »Laboratory – biomass burning« and »Payerne – winter« data. For low Ångström exponent the situation is more complicated as shown and discussed later in the article. We have modified the text to make the message clearer (lines 266-269):“Table 1 also reports the average values of the absorption Ångström exponent obtained for each campaign. Occurrence of higher k values appears to be linked to ~~the latter parameter~~higher values of the absorption Ångström exponent, which is commonly used as a tracer for biomass burning aerosols (Kirchstetter et al., 2004; Sandradewi et al., 2008).”

- P. 10 line 277 and Table 2: a figure (see thereafter) seems much more appropriate than a table to see the correlation between AAE and k6. Looking at the figure, I do not understand why you say that April, May and October (with a red circles) are exceptions. I'm aware that I did not report the errors on the figure, but the correlation seems otherwise to be ok.



ResponseRC1.13: The correlation plot has been added to the article supplement:
"**S.5 Seasonal variation of filter loading effect – Paris campaign**

Figure S5 shows dependency between filter loading parameter parameter k_6 and absorption Ångström exponent for monthly averages listed in Table 2.

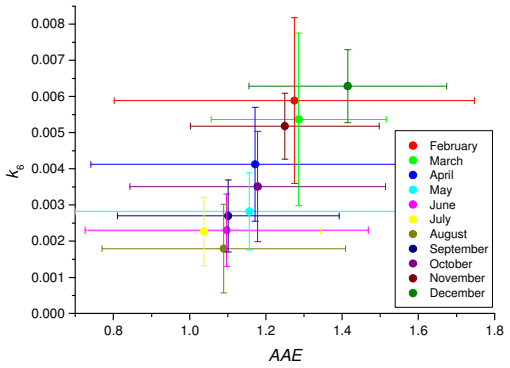


Figure S5. The correlation between the FLE compensation parameter k_6 and the absorption Ångström exponent *AAE* for monthly average values and standard deviation obtained during 2013 Paris campaign (SIRTA observatory)."

In general it holds that k_6 is correlated with *AAE*. If we focus solely on averages for April, May and October we can observe big variation in k_6 (0.0028 – 0.0041) with no significant difference in *AAE* (1.16 – 1.18). This means that *AAE* is not the only factor responsible for variation of k_6. As noted in the text there are two distinct factors influencing k_6 – both are analyzed in detail later in the article. The dependency of k_6 on Ångström exponent is

investigated for the winter period (Figure 5). Secondly, the data are investigated depending on the coating factor (Figure 8).

- P. 11 line 289: k6 decreases with AAE for AAE>1.2. For AAE<1.2, it is not sure.

ResponseRC1.14: We agree. Text is changed to (lines 321-322):"The results confirm that for AAE values above ~~higher than~~ 1.2 the loading parameter k_6 increases with ~~the~~ *AAE* (Figure 5), indicating higher values for biomass burning emissions compared to traffic emissions."

- P.14 lines 361-369: can the observed time lag between k6 and CF be also due to the time taken by the gaseous species to coat the aerosol particles ?

ResponseRC1.15: That is an interesting hypothesis. Particles caught in the filter tend to be in equilibrium with the gas phase. During summer, the sample temperature is similar to the ambient temperature; that is why we do not expect a higher condensation rate compared to the ambient particles.

- P.17 lines 416-418:please rephrase! The fact that the PBL is thicker in summer than in winter is obvious and does not need a reference. The fact that there is a stronger influence of long-range transport than in winter is not obvious at all and should be referenced. The end of the sentence is somewhat curious.

ResponseRC1.16: The whole chapter has been modified. Please see the Response RC1.18 below.

- P.17 line 420 and 421: k6 instead of k?

ResponseRC1.17: The text was updated with "k_6" instead of "k". The text was further modified – please see the Response RC1.18 below.

- Figure 9 + explanation in text: the number of cases for k2 lower and higher than 0.002 is not mentioned. In case of a large difference of cases, the seen effects could be only due to the amount of data. Since no figures for low BC and CF concentrations are given, it is also not possible to be sure that the pattern would be clearly different than the ones for high BC and CF concentrations. For Payerne, the differences for low and high k6 are not obvious. Moreover, I'm not convinced by the term "regional" asking myself if great-Britain and the Atlantic ocean can be considered as in the region of Paris.

ResponseRC1.18: For both sites, Paris and Payerne, $k_6 > 0.002$ and $k_6 < 0.002$ occurred around 60% and 40% of the time, respectively. The data are therefore ~~-~~representative. This information has been added to the text. As pointed out, our interpretation of the PSCF results may have been too direct. We have re-thought the corresponding paragraph in order to tone down our reasoning, given that using backtrajectories on a pollutant which can be emitted locally may limit the interpretation. The term "regional transport" was replaced with "long-range transport". Section 3.5 was modified to (lines 453-501):

"Influence of the aerosol age was indirectly investigated by using potential source contribution function (PSCF). We divided the dataset into two subsets distinguished by k_6 being bigger or smaller than the campaign average of 0.002. The analysis was carried out for the summer period at Paris and Payerne (Figure 9). For both sites, $k_6 >$ 0.002 and $k_6 <$ 0.002 ~~occured~~occurred around 60% and 40% of the time, respectively. ~~, meaning that t~~There is sufficient data in both subsets to provide comparable results.~~The analysis was carried out for the summer period, when the planetary boundary layer is thicker compared to the winter with stronger influence of long-range transport than in winter, and good vertical mixing to the ground, where the measurement station is positioned.~~

In Paris, the compensation parameter k_6 is very well correlated with aerosol age: high values indicate local sources while values close to zero indicate ~~a~~ long-range transport (Figure 9).~~,~~ ~~h~~High k_6 values are associated ~~to~~with a local pattern of air pollution, since highest PSCF values are located near the station. The map resembles ~~to~~results ~~what has been,~~ previously obtained in Paris for local sources like traffic and wood burning (Bressi et al., 2014). Measurements during the MEGAPOLI campaign showed that fresh traffic BC particles are non-coated, whereas BC particles from long-range transport exhibit substantial coatings of non-refractory material (Laborde et al., 2013). For low k_6 values ~~For~~ ($k_6 < 0.002$) the sources are distributed over France, part of Great Britain, and the Atlantic Ocean.~~, PSCF highlights different regions of France, which are not usually linked with long-range transport. Indeed, advected BC have been shown in Paris to be associated with Northernly and/or North-Easterly air masses (Healy et al., 2012). But~~ PSCF results for *CF* follow the same pattern, ~~so may still~~ indicating ~~e~~ a

potential coating material that is brought to Paris by mid- and long-range transport during which the emissions are aged and aerosols get coated, and also mixedalso with more local sources of BC (Bressi et al., 2013; Petit et al., 2015).

~~In Paris, the compensation parameter k is very well correlated with aerosol age: high values indicate local sources while values close to zero indicate a regional contribution (Figure 9). For low k_6 values it seems that the sources are distributed over France, part of Great Britain, and the Atlantic Ocean. This fact may be explained by influx of potential coating material that isair masses brought to Paris by mid- and long-range transport during which the emissions are aged and aerosols get coated, and which are then mixed with more local sources of black carbon (Bressi et al., 2013; Petit et al., 2015). In Payerne, the meteorological situation is different having a smaller source area. This can be explained by the station being located between the Jura mountains and the Alps where the air is in general more stagnant compared to Paris, and is channeled from southwest to east-northwest due to the mountain ranges. Still we can observe that low k measurements are related to distributed sources further from the station. At both locations, the distribution of the coating factor resembles that of the low k_6. This is in agreement with the correlation analysis in the chapter above, where k_6 decreases with CF (Figure 8, A, B). A low value of k_6 is indicative of aged particles, and a high value of fresh, local aerosols. This is in agreement with the spectral fingerprint of fresh diesel engine emissions (Figure 1). Measurements in Paris during the MEGAPOLI campaign showed that fresh traffic BC particles are non-coated, whereas BC particles from long-range transport exhibit substantial coatings of non-refractory material (Laborde et al., 2013). On average, regional transport contained 7 % of EC mass compared to 37 % from local emissions (Healy et al., 2013), in accordance with our PSCF analysis of the coating factor.~~

Theoretical studies show that coating consisting of secondary organic and inorganic species is mostly transparent in the visible part of the spectrum and can affect the absorption of light by the particles (Fuller et al., 1999; Bond et al., 2006). The fact that coating can increase absorption was confirmed in ambient studies (Wei et al., 2013b; Liu et al., 2015) and the coating may also be responsible for the decrease of parameter k_6; -the possible mechanism would be the increase in SSA and decrease of the backscatter fraction caused by the coating (Virkkula et al., 2015). In Payerne, the discrepanciesdifferences between high and low k_6 are not clearly appreciable, which can be explained by a different meteorology and orography. Indeed, the station beingis located between the Jura mountains and the Alps where the air is in general more stagnant compared to Paris, and is channeled from southwest to east-northwest due to the mountain ranges. This limits the interpretation of our PSCF results, and should be further investigated on a largerlonger temporal scale (e.g. several months), which would provide more representative results for this station."

- P.17 line 422-424: I think that the causality link is just inverse: the trajectories explain the presence of coating material.

ResponseRC1.19: Text is changed to (lines 470-473):" PSCF results for CF follow the same pattern, ~~so may still~~ indicatinge a potential coating material that is brought to Paris by mid- and long-range transport during which the emissions are aged and aerosols get coated, and also mixedalso with more local sources of BC (Bressi et al., 2013; Petit et al., 2015). "

- Fig. 10: to which kind of sample corresponds image C? I do not see the white arrows described in the text.

ResponseRC1.20: Figure 10 caption is changed to (lines 530-534): "**Figure 10: SEM images of ambient (A, C) and thermo-denuded (B) impactor samples (size range 170 – 260 nm) taken during the Ljubljana campaign. The energy-dispersive X-ray spectra (D) were obtained at the selected areas on image (C). Red and yellow arrows mark soot agglomerates and secondary ammonium sulfate residues, respectively.**". The description in the text was modified (lines 538-540): "We can observe soot agglomerates (white patches marked by~~,~~ red arrows), organic residues (dark patches around agglomerates), and brain-shaped dendritic residues (marked by yellow arrows)."

- Fig. 11 b is not necessary.

ResponseRC1.21: We have removed Figure 11b~~ is removed~~. The figure caption is updated (lines 565-567): "**Figure 11: Influence of dried and/or thermo-denuded ambient aerosols on the filter loading parameter k_6 - ~~:~~ diurnal plot. ~~(A) and campaign averages (B).~~ Average values of k_6 for different treatments are significantly different with $p = 0.05$.**"

- P. 21 last §: why the soot particles begin to age by developing a coating immediately after sunrise? Is it an effect of solar radiation? Or an effect of concentration of soot particles and secondary

species (and their relative content) ? how do you explain the k6 diurnal cycle of ambient aerosol? Is the concentration of secondary species larger in the end of the afternoon?

ResponseRC1.22: Immediately after sunrise, soot particles in the atmosphere begin to age by developing a coating of secondary species including ammonium nitrate, sulfate, and organics (Moffet and Prather, 2009). We attribute the ageing and coating of the soot particles to photochemistry. Additionally, increased and solar radiation driven vertical mixing brings aged particles form the residual layer to the ground during the day. These two effects result in coated soot at ground level featuring larger diameters than the freshly emitted particles. Strong vertical mixing in the afternoon (12h – 18h) caused a reduction of *BC* (Figure S4.A). We observed an increase in particle diameter during that period (Figure S4.B). The k_6 diurnal profile might be shifted to the right because of the lag, similar as in Figure 7.

How do you explain the increase of the diurnal cycle after drying ?

ResponseRC1.23: The daily variation of k_6 is larger for dried sample compared to the ambient. This might be related to higher magnitude of k_6 for the dried sample (0.005 compared to 0.003). The relative variation is similar for both treatments.

- P. 22 lines 528-530 see major comments

ResponseRC1.24: In the conclusions (lines 528-530) we state: "The filter loading parameter value increases with the absorption Ångström exponent. It is suggested that this effect is related to the size of the black carbon agglomerates." We believe our notion is adequate. Please see our reply above.

- P. 22 lines 534: the main effect of the coating effect and therefore of the difference between summer and winter measurements is to my point of view not the reduction of the filter loading effect (not much is visible at 350 nm) but the modification of the k wavelength dependence.

ResponseRC1.25: Throughout the article we are talking about the variation of filter loading effect in the infrared part of the spectrum. Virkkula et al (2015) have shown that the value of k_6 and the wavelength dependence of k (as parametrized by a linear slope a_k) are homologous. In the UV and blue the difference between winter and summer is much smaller – see Figure 4 for example. Section 3.2 is modified to (lines 291-298): "Concomitantly with the absorption Ångström exponent, the parameter k shows large seasonal variations (Figures 3 and 4). Virkkula et al. (2015) analyzed ~~parameter~~the k wavelength dependence~~variation~~ by calculating the slope of k *vs.* λ.~~;~~ ~~I~~It was shown that slope is ~~very~~extremely well correlated with the compensation parameter k_6 (measured at 880 nm), ~~which can well enough~~so either of the two can be used to describe the variation of parameter k. For the sake of simplicity, we ~~will~~ focus our further analysis on k_6. ~~Our investigation is focused here on k_6 (λ = 880 nm), because of larger k variability at longer wavelengths (Drinovec et al., 2015; Virkkula et al., 2015), and since Aethalometer measurements at 880 nm are traditionally used for the determination of black carbon mass concentrations.~~"

References

Müller, T., Virkkula, A., and Ogren, J. A.: Constrained two-stream algorithm for calculating aerosol light absorption coefficient from the Particle Soot Absorption Photometer, Atmos. Meas. Tech., 7, 4049-4070, doi:10.5194/amt-7-4049-2014, 2014.

Virkkula, A., Mäkelä, T., Hillamo, R., Yli-Tuomi, T., Hirsikko, A., Hämeri, K., and Koponen, I. K.: A simple procedure for correcting loading effects of Aethalometer data, J. Air Waste Manage., 57, 1214–1222, doi:10.3155/1047-3289.57.10.1214, 2007.