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

REVIEW

GENERAL

In this paper the authors have analyzed the information that can be obtained from the filter loading parameter that the new aethalometer model outputs in addition to BC concentration. The paper presents field and laboratory measurements of various light-absorbing aerosols and discusses factors affecting the loading parameter. The paper is in general easy to read and the results will surely prove out to be very useful for the community measuring BC. I can recommend publishing the paper with minor revisions.

The most significant misunderstanding is already in the title of the article. The data indeed suggests that the loading parameter depends on the size and coating of the BC particles and thus their age but there is no evidence of that it would depend on the mixing state. Fig (6) shows that k6 has very different values as a function of the coating factor defined in eq. (3) in winter and summer, that is true. On line 396 it is written that in winter aerosol is more externally mixed, which is very probably true also. The next argument is not. It is argued that since k6 is higher in winter it is due to the state of mixing. Why would in not be due to the thinner coating of the BC particles? After all, they are the particles that affect light transmittance most in the filter medium. Let us assume that the aerosol is an external mixture of light-absorbing and scattering particles. To show that the factor that affects k6 is really the state of mixture and not the coating of the light-absorbing (= BC, here) particles, the light-scattering particles should be removed without affecting the coating or any other property of the BC particles. So that only the state of mixing would change. Doing that would prove that it is the state of mixing that affects the k6. The thermodenuder field experiment, section 3.6, shows that after heating and drying the sample air the k6 is higher. Again, this is no evidence of the effect of the mixing state on k6. By heating the sample air the externally-mixed light-scattering particles get removed but also the coating of the BC particles gets thinner or totally removed. As a result, the size of the light-absorbing particles decreases which leads to changes in the penetration depth into the filter and also increase in backscatter fraction which is inversely proportional too the particle size. And then k6 grows. So I claim that the change of k6 is more probably due to the change of the coating of the BC particles and not due to the removal of the purely light-scattering particles, i.e., change of the mixing state.

Actually, I can't really find any other way to prove that k is affected by the state of mixing alone but to make an external mixture of scattering and absorbing aerosol: first measure pure BC particles from a chamber for a while, then blow in also scattering aerosol and keep measuring. If k changed just due to the addition of scattering aerosol, the title of the paper would be true. The evidence from the experiments presented in the paper rather only suggest that the loading effect depends on the coating of the light-absorbing particles. I strongly suggest changing the title accordingly. Also in the conclusions it is written "*Our results show that the filter loading parameter can be used as a proxy for determination of the particle mixing state, thus allowing to differentiate between local/fresh and transported/aged particles* ". Based on my above argumentation I would remove the statement about mixing state but it can be used to differentiate between local/fresh and transported/aged aerosols.

ResponseRC2.1: We thank the reviewer for pointing this out. There might be some misunderstanding about the definition of the mixing state. We have followed the definition from Seinfeld and Pandis

(2006), which describes two possible mixing states: external mixture, where there are two populations of absorbing and non-absorbing particles and internal mixture with one population of particles, which are a homogenous mixtures of absorbing and non-absorbing components. Because black carbon material cannot be homogenously mixed with non-absorbing material there is in practice a core-shell mixture configuration that was predicted in our article. Core-shell configuration was defined as a third mixing state by Jacobson (2000, 2001) who showed that optical properties of core-shell mixing state are somewhere in between two extreme case of external and (homogenous) internal mixture. To clarify this issue we included the definition in the Introduction section and used the 3 state model throughout the article. We have incorporated the reviewer's suggestions as follows:

Title is changed to
"**The filter loading effect by ambient aerosols in filter absorption photometers depends on the ~~mixing state~~coating of the sampled particles**"

In the Introduction section the following paragraph is added (lines 97-103):
"There are two extreme mixing state models: ~~an~~of internal and an external mixture as defined by Seinfeld and Pandis (2006), where the external mixture represents two separate populations of two types of particles and where an internal mixture represent one population of particles composed of a homogenous mixture of materials ~~form~~from the two types. Because black carbon cannot be homogenously mixed with non-absorbing material, a third mixing state: ~~of~~a core-shell state was introduced (Jacobson 2000). We use the term "mixing state" to refer to either of these states, most notably the external and the core-shell. "

The abstract is modified as follows (lines 33-35):
"In this paper, we investigate the hypothesis that this filter-loading effect depends on the optical properties of particles present in the filter matrix, especially on the black carbon particle ~~mixing state~~coating."
and (lines 47-49):
"Our results show that the filter-loading parameter can be used as proxy for determination of the particle ~~mixing state~~coating, thus allowing for differentiation between local/fresh and transported/aged particles."

The Conclusions are updated to (lines 605-606):
"Our results show that the filter loading parameter can be used as a proxy for determination of the particle ~~mixing state~~coating, thus allowing to differentiate between local/fresh and transported/aged particles."

Detailed comments

P4, L111. " The absorption coefficients are calculated" How are they calculated? What Cref? Based on what? Any scattering corrections?

ResponseRC2.2: All Aethalometer based calculations follow the article Drinovec et al. 2015. As the reference is already stated several times in the Instrumentation section we changed only the first sentence (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)."

Multiple scattering parameter *C* = 1.57 was used and no scattering correction was applied, as the cross-sensitivity to scattering is small (Drinovec et al., 2015).

P5, L135-143, Description of the electron microscopy. What compounds and/or elements were obtained? How many particles were analyzed?

ResponseRC2.3: We have performed a qualitative analysis on several particles. Typical spectra are presented in Figure 10. The Instrumentation section was modified (lines 161-164):

"Representative areas were chosen for further EDX analysi~~es~~, which was focused to the identification of the coating material of soot agglomerates. The microanalysis was performed at 10 mm WD with acquisition time of 50 to 150 s. Since the spatial resolution of EDX analyses is around 1 µm, the obtained results were considered only in terms of elemental compositions and not their ratios."

You also present single-scattering albedo later. How was scattering measured? Describe also its measurement. What was the time resolution of each instrument?

ResponseRC2.4: Single scattering albedo was measured during Reno laboratory experiment using the Photo-Acoustic Soot Spectrometer (model PASS-3, Droplet Measurements Technologies). The paragraph describing Reno experiment has been updated (lines 212-224):

"The Reno laboratory experiment was conducted at Desert Research Institute (Reno, Nevada, USA). Pure mustard oil was burned in a simple ceramic bowl with a cotton wick. The diluted emissions were collected and injected into a distribution chamber (50 l) from which the sample was routed to multiple instruments: ~~Aethlometer~~the Aethalometer model AE33 run at 1 s time resolution, the Photo-Acoustic Soot Spectrometer (model PASS-3, Droplet Measurements Technologies) operated with 2 s time resolution, and the SMPS (TSI, DMA model 2080 with CPC model 3775). ~~ ~~Ponderosa pine needles (~ 50 grams) were combusted in a biomass combustion chamber, a close replica of which has been described by Tian et al. (2015). The combustion process could be divided in the flaming and smoldering phases. Focusing on the flaming phase, we injected the emissions from the first 35 ~~seconds~~ of the combustion into the distribution chamber. The sample from the distribution chamber was analyzed for approximately 15 minutes. ~~The emissions from the first 35 seconds of combustion were collected in the distribution chamber and analyzed by a SMPS (TSI, DMA model 2080 with CPC model 3775) and an Aethalometer (model AE33).~~ PASS-3 absorption and scattering measurements ~~data~~ ~~was~~were used to calculate the *SSA* (Lewis et al., 2008)."

P6, L193: "... was routed to multiple instruments." Which instruments? The first 35 seconds of combustion was measured. Why so short? Was the burning at any kind of stable state then? I assume aerosol concentrations simply decreased. How long did you measure? Time resolution?

ResponseRC2.5: The experiment was described in more detail (please the ResponseRC2.4). The injection of flaming emissions into the distribution chamber allowed us to perform the measurement focusing on the flaming phase for a prolonged period until the aerosol concentrations in the distribution chamber was greatly reduced.

P10, Table 2. Why don't you also give the wavelength dependency of the k1 – k7 in the results? This applies also to the other result tables and figs.

"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.~~ High values of k_6, between 0.006 and 0.012 are observed during winter, while in summer k_6 remains low, ~~with~~featuring still large oscillations (0 – 0.005), with episodes of low k_6 that can last for several days, indicating stronger influence of weather conditions than of daily cycles."

P12, L308: "… mean mobility diameter…" which mean? Geometric? Arithmetic? Volume or number?

"Mustard oil burning produces particles with a mode of ~~mean~~ mobility number size distribution~~diameter~~ of 210 nm (Figure 6A), which compares fairly well with the median aggregate mobility diameter of 29~~76.8~~ ± 7~~43.9~~ nm reported by Chakrabarty et al. (2013) for mustard oil lamp emissions."

p12, L311 – 313. When comparing AAE you should use as similar a wavelength range as possible (cf. Lack & Cappa, ACP 10, 4207–4220, 2010, Fig 8). How would your AAE be using 370 – 880 nm?

P13, Fig 6b. Give units for y axis. Why do you use aerodynamic diameter if you measured with an SMPS? To calculate aerodynamic diameter from mobility diameter you need density. What did you use?

"**Figure 6: The filter loading parameter k for laboratory measurements of emissions from mustard oil lamp and flaming Ponderosa pine needles (A). ~~Normailzed~~Normalized ~~a~~Aerosol number size distributions for both sources (B).**".

How high was the mustard oil nucleation mode? Now the y axis is limited. True, particles smaller than 20 nm contribute little to absorption and especially scattering but if there are very many of them they may affect the aethalometer. You could calculate the contribution of the two modes to absorption. The two mustard-oil modes are probably chemically and thus also optically different. Comments on that?

ResponseRC2.10: The combustion emissions were first diluted and then led into the distribution chamber. We expect the soot to agglomerate by the time it is sampled into the instruments. Small particles (20 nm) are probably mustard oil droplets, and big particles (mode 210 nm) soot agglomerates. Due to the low *SSA* (*SSA*=0.22), we do not expect much interference with the Aethalometer measurements.

P13, Table 3. What mean diameter? GMD? Give also the width as GSD. Please make one more figure that shows time series of the lab experiment data.

ResponseRC2.11: In Table 3 we presented the mode of number size distribution. The Table 3 caption is updated (lines 376-378): "**Table 3. Filter loading parameter k_6, ~~mean~~ aerosol mobility diameter (mode of number size distribution), single scattering albedo *SSA* at 532 nm and ~~-~~absorption Ångström exponent *AAE* of soot generated by mustard oil lamp and flaming Ponderosa pine needles.**"
The time series of the laboratory experiments was added to the article supplement (lines 80-89):
"**S.6 Reno experiment *BC* time series**

Figure S6 shows time series for mustard oil lamp and flaming needles emission measurements. For the mustard oil lamp it was possible to continuously inject diluted emissions into the distribution chamber. For the flaming needles experiment, the flaming emissions were injected into the distribution chamber. When air was drawn into the instruments, the aerosol concentrations decreased exponentially.
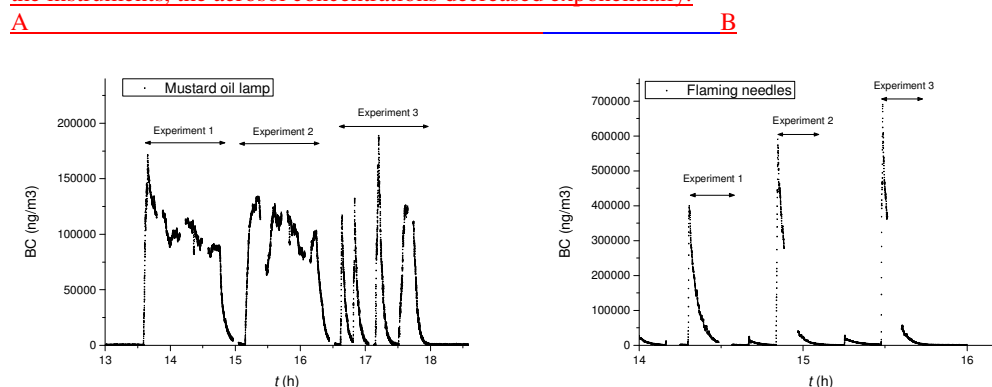A   B

Figure S6. Time series of *BC* during the Reno laboratory experiments for mustard oil lamp (A) and flaming needles (B) emission measurements."

P17, L439: "... the coating may also be responsible for the decrease of parameter k." And coating probably also increases SSA and decreases backscatter fraction. Consistent with Virkkula et al. (2015)

ResponseRC2.12: The reviewer is correct. The changes in *SSA* and backscatter fraction are expected to change the light intensity distribution in the filter matrix. This might be a mechanism of how the coating influences the filter loading effect. The text was updated (lines 493-496):
"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; ~~-~~the possible mechanism would be the increase in *SSA* and decrease of the backscatter fraction caused by the coating (Virkkula et al., 2015)."

And one more comment: Reviewer 1 writes "*to my knowledge, there is no dependency of the AAE to the aerosol size (or size distribution).*" Sure particle size affects also AAE. It is easily modeled and has been published, e.g., by Gyawali &al, ACP 9, 8007–8015 (2009); Lack & Cappa, ACP 10, 4207–4220 (2010)

ResponseRC2.13: We thank Reviewer 2 to point Reviewer 1 to the references on *AAE* and particle size.

References

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