

Interactive comment on “Aerosol light absorption from attenuation measurements of PTFE-membrane filter samples: implications for particulate matter monitoring networks” by Apoorva Pandey et al.

W. White (Referee)

whwhite@ucdavis.edu

Received and published: 29 August 2018

GENERAL COMMENTS

This discussion paper compares optical measurements of PTFE-membrane filter samples with in situ measurements of the aerosols from which they were collected. It is novel in its approach and inspiring in its ambition. The authors generated carbonaceous aerosols with a range of optical properties from the combustion of biomass fuels and kerosene, using an integrated experimental system to collect paired in-situ and

C1

filter-based optical data. A virtual AOD (absorption optical depth) was calculated for each sample, as the product tau of the in-situ photoacoustic absorption coefficient and the length of the sampled air column. The sample's actual AOD was independently estimated from direct measurements of overall filter reflectance and transmittance, presumably with a single or double integrating sphere system that is not described. The authors summarize the empirical relationship between the two absorption measures with a “best fit” formula they motivate as “established in conjunction with” predictions from a two-stream radiative transfer model.

It feels awkward for me to comment as a referee on the titular “implications for particulate matter monitoring networks”, which is based on a “case study” of the IMPROVE haze monitoring network. Having coauthored a recent paper (White et al., 2016) validating the filter-absorption measurement reported by IMPROVE, I may be viewed as conflicted when evaluating this discussion paper's interpretation of those data. It seems fair, however, to observe that no one should expect the absorption characteristics of an agglomerated deposit of particulate matter to be exactly those of the morphologically complex and often fragile aerosol particles from which it was filtered. Figures 2 and 3 indeed show a great deal of scatter in the relationship between these two measurement types, even when obtained within the same laboratory system by the same investigators. The discussion paper undertakes to produce an empirical calibration for a specific filter-based measurement in terms of in-situ aerosol measurements. Its finding, that applying the same calibration to a completely different measurement system in Figure 5 produces an unsatisfactory relationship, should not surprise anyone who recalls the authors' earlier comment (page 2, line 16): “Typically, correction algorithms . . . are specific to a given measurement system.” Moreover it is misleading to call this foreign calibration of IMPROVE data a correction: the designation of IMPROVE data as Fabs rather than babs is explicitly “intended to remind users of {their} origin in a filter-based measurement” (White et al., 2016), with an explicitly noted bias estimated in the range $1 \leq \text{Fabs/babs} \leq 2$.

C2

The questions and concerns raised below about the filter-based measurements at Washington University, and their relationship to the IMPROVE measurement, could be directly addressed by reanalyzing the same sample filters on the HIPS system used at UC Davis for the IMPROVE measurements. The ability to revisit previously analyzed samples is an important strength of filter-based absorption methods, and both laboratories could learn by taking advantage of this opportunity. A comparison between the WUSTL in-situ measurements and UCD HIPS results may have only limited relevance for the predominantly rural and remote IMPROVE network, which among other differences samples generally mixed and well-aged emissions rather than strictly fresh fumes and smokes. The HIPS group, with whom I am in contact, would nevertheless be delighted to collaborate in exploring the possibilities.

SPECIFIC COMMENTS

1. The entire description of the authors' filter optics measurements is a scant two sentences: "Transmittance (T) and reflectance (R) for the filter samples were measured using a Perkin-Elmer LAMBDA 35 UV-vis spectrophotometer (described in Zhong and Jang (2011)). Attenuation (ATN) through the filter samples was calculated using (Bond et al., 1999; Campbell et al., 1995): $ATN = \ln((1-R)/T)$ ". This hardly specifies what was measured, as detailed in the next two questions below.

(a) Which "R" are we talking about here? Is it the reflectance of the "dirty" side of the filter, as in the old British Smoke Shade (BSS) method? This is what the 2011 Zhong and Jang reference indicates in its Figure 1b. Or is it the reflectance of the "clean" side, as specified in the 1995 Campbell et al. paper ("All measurements were made with the side of the filters containing the particle deposit facing away from the laser beam") and continued in all subsequent IMPROVE measurements (White et al., 2016)? For a moderately loaded sample filter, the difference is apparent to the naked eye. Moreover, light reflected from the "dirty" side depends nonlinearly on the AOD: the portion reflected from the pristine layer of substrate must pass twice through the deposit layer, creating a quadratic dependence on the particle loading (cf. Equation

C3

4, Gorbunov et al., 2002). The fact that this quadratic dependence appears in the discussion paper's radiative transfer model (Equation 6B) implies R was measured on the sampled side of the filter.

(b) What light-collecting geometry was used to measure R and T? On the one hand Zhong and Jang (2011) describe separate measurements of T and R, with a single integrating sphere accessory operated in two different configurations. This resembles the LISA (Laser Integrating Sphere Analysis) described by Campbell et al. (1995). On the other hand the 2016 paper by Pandey, Pervez, and Chakrabarty, which seems to be a precursor to the paper under review, describes using a PerkinElmer LAMBDA 35 – the very same instrument? – with a double integrating sphere system to make the same kind of measurements. These two arrangements require different approaches to interpreting and calibrating the raw data: jointly measured T and R signals from a pair of integrating spheres (e.g. Pickering et al., 1992), or from the hybrid of integrating sphere and plate used by IMPROVE (White et al., 2016), are coupled in ways that successive measurements of the individual signals are not.

2. Light attenuation through a filter sample is generally defined as $ATN = \ln(T_b/T_s)$, where T_b is the transmittance of the unsampled filter blank and T_s is that of the same filter after sampling (e.g. Pandey et al., 2016). The alternative measure $\ln((1-R)/T)$ introduced by Campbell et al. (1995) uses the reflectance R_c of the sampled filter's "clean" (unexposed) side as an estimate $R_c \approx R_b$ for the reflectance of the unexposed blank. The expectation that bare PTFE does not absorb, so that $T_b = 1 - R_b \approx 1 - R_c$, then justifies the substitution of $\ln((1-R_c)/T_s)$ for attenuation as usually defined. It should be noted that Campbell et al. (1995), Bond et al. (1999), and White et al. (2016) all refer to $\ln((1-R)/T)$ as a measure of AOD rather than attenuation. I think this discussion paper's unannounced and unmotivated change in terminology is likely to introduce confusion in the majority of readers who are not familiar with the rationale just outlined. And again, this rationale strictly requires that reflectance be measured for $\ln((1-R)/T)$ on the "clean" $R = R_c$ side of the sampled filter; it's not clear what relevance the quantity $\ln((1-R)/T)$

C4

would have to attenuation or any other interesting sample property if R were measured on the side darkened by the collected sample deposit.

3. The experimental program described in this discussion paper was well designed to test our standard accounts of radiative transfer in filter samples, providing real data for a closure study that I have not seen attempted before. The authors have produced 75 experimental filters according to Table S1, presumably running each through their spectrophotometer system before sample collection to characterize the substantial variability in individual PTFE membranes that was highlighted by White et al. (2016). They have modeled radiative transfer through the filter at an appropriate level of detail, and have measured relevant optical properties of both the aerosols and collected particulate matter. They have suggested plausible estimates for unmeasured parameters such as penetration depth and scattering asymmetry. The sampled aerosols were each characterized at three different wavelengths, which should yield $3 \times 75 = 225$ independent sets of model data inputs. I was expecting these substantial interwoven efforts to culminate in illuminating comparisons, presented in formats such as scatterplots of modeled vs. measured R, T, and ATN. Absent any clear link to the measurements, what was the intent of the modeling?

4. Relatedly, in what sense is Equation 7 a “best fit” to the observed relationship between ATN and AOD? What does it mean to say “the nature of this function was consistent with predictions from a two-stream radiative transfer model”? Is Equation 7 simply an OLS regression of logarithms, or is it somehow informed by results from the radiative transfer modeling? What sort of functional form does the two-stream model predict when it is run over a wide range of sample loadings from a representative aerosol of fixed optical characteristics?

5. The only results I see explicitly attributed to the two-stream model are the colored wedge shapes in Figure 2. I don’t understand why these don’t show y-axis ATN declining toward zero, the model prediction for a blank, as the virtual absorption optical depth of the aerosol sample approaches zero on the x-axis.

C5

6. The two-stream radiative transfer modeling framework presented here, along with its hyperbolic solutions, is widely known also as Kubelka-Munk theory, after an extensive older literature arising in paper and paint research (e.g. Kortum, 1969). Referencing this connection in passing might attract a few additional readers.

TECHNICAL CORRECTIONS

Line 25, page 6 of main paper: The reference to Figure 1 appears to be in error.

Section S4 of supplement: (a) In the IMPROVE network, the equivalent length of the sampled air column can vary somewhat from sample to sample. The 93 km value is a design target, subject to limited and occasional flow and timing variations, and is not “fixed”. (b) The IMPROVE data warehouse at CIRA holds Fabs and EC values from 2010 for 172 sites; in no year has the network ever operated 223 sites. (c) Authors who use IMPROVE data are asked, as a favor to aid in tracking these papers, to include the seminal 1994 paper by Malm et al. as a reference.

REVIEW REFERENCES NOT ALREADY INCLUDED IN THE DISCUSSION PAPER

G. Kortum (1969) *Reflectance Spectroscopy: Principles, Methods, Applications*. Translated from the German by J.E. Lohr, Springer-Verlag New York.

W. C. Malm, J. F. Sisler, D. Huffman, R. A. Eldred, and T. A. Cahill (1994), Spatial and seasonal trends in particle concentration and optical extinction in the United States, *J. Geophys. Res.*, 99, 1347-1370.

J.W. Pickering, C.J.M. Moes, H.J.C.M. Sterenborg, S.A. Prah, and M.J.C. van Gemert (1992) Two integrating spheres with an intervening scattering sample. *J. Opt. Soc. Am. A*, v9, pp. 621-631

ACKNOWLEDGMENT Scott Copeland, a coauthor of the original Campbell et al. (1995) paper, helped focus my thoughts by noting the important distinction between calibration and correction.

C6

