

## ***Interactive comment on “Evolution of multispectral aerosol optical properties in a biogenically-influenced urban environment during the CARES campaign” by M. Gyawali et al.***

### **Anonymous Referee #2**

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Gyawali et al. present measurements from the 2010 CARES study that took place around Sacramento, CA. They focus on differences in aerosol optical properties observed between two sites: one located in the city and one located further downwind. Through this, they aim to understand how photochemical processing affects the particle optical properties, with a particular emphasis on the formation of so-called brown carbon. They also focus on contributions from supermicron particles to the observed scattering. The latter story is mostly disconnected from the former.

My main concern at this point, and that actually limits my ability to decide whether this paper is potentially publishable or not, is that I find the consideration of uncertain-

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ties to be exceptionally weak, almost nonexistent. In a study that aims to investigate differences between measurements made at two sites using a multitude of different instrumentation, explicit characterization and description of the uncertainties involved for all of the methods, and appropriate application and consideration of such uncertainties is required to draw meaningful conclusions. I believe that this manuscript should be reconsidered (i.e. re-reviewed) after the authors are given an opportunity to address this primary issue. Many of my specific comments stem from this concern.

### Specific comments

Section 2.2: Given the many different wavelengths involved, and the multiple instruments involved, the authors should provide information on the basic calibration procedures used and must state explicitly the absolute % uncertainty at every wavelength for both scattering and absorption. Only finally on P7131 do I find any mention of uncertainties (stated as 5% for absorption and 15% for scattering), but it is not clear whether these are appropriate for this study at all wavelengths since no information on calibration methods is provided.

Section 2.2: The authors indicate that absorption and scattering measurements were made at many wavelengths, but then only 3 wavelengths are considered for SSA determination at each site (and not the same 3). What is the reason for this? Similarly, why are similar pairs of wavelengths not used at the two sites for AEA determination? I understand they say that they want to emphasize light absorption by organics, but by at least comparing results between the two sites with the same wavelength pairs, one would be potentially able to more easily assess differences. The consideration of a non-matched wavelength pair could then be used to provide more in depth understanding. I do not believe it is appropriate to quantitatively compare the AEA values determined for different wavelength pairs. Similarly, if fits are performed (as in Fig. 7) using different wavelengths, then the results are not comparable.

Is there a potential for absorption by gas-phase species at UV wavelengths?

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Section 2.3: Regarding the correction of the [rBC] to account for the use of Aquadag as a calibration standard, the authors multiply by 1.6, but if one looks at the “Slope of linear fit” from Moteki and Kondo (2010) for Aquadag and ambient soot, the ratio should actually be 1.32. The ratio between Aquadag and Fullerene soot is 1.42. Both are smaller than the factor of 1.6 applied here. Laborde et al. (2012) similarly find a smaller ratio than 1.6 (they find the ratio is size dependent, with a value of 1.3 for a particle of 10 fg rBC).

P7122: Technically, the APS aerodynamic diameter to spherical-equivalent diameter adjustment should also include the change in the particle slip correction, which is size dependent.

Figure 7: I find that this figure does not properly account for/present the uncertainties associated with the measurements. The authors plot their derived mass absorption coefficients (MAC) vs. wavelength to assess the influence of wavelength on light absorption. The error bars they include are derived from the fit error to a plot of babs vs. [BC]. These error bars do not present a true indication of the actual uncertainty in the measurements made at each individual wavelength, and in fact substantially underestimate the actual uncertainty. Consider that the apparent uncertainty on the 870 nm MAC at T1 is 0.08 out of 5.57 Mm<sup>-1</sup>, which is a percent uncertainty of 1.43%. Neither the absorption nor the [BC] measurements are good to within 1.43%. However, recognizing that all of the absorption measurements are effectively divided by a “constant” (i.e. the [BC] time series), uncertainty in [BC] can, for the time being, be ignored. Then the actual uncertainties should simply be the absolute uncertainty associated with the absorption measurement at each wavelength. These will be wavelength specific. This is particularly important because the AEA determination depends on the accuracy of the measurements at the different wavelengths, not their precision. I believe that it is important that this figure indicate the absolute uncertainty, and not the fit uncertainty. Errors should be propagated accordingly. Further, given that [BC] is a constant (by which I mean all the absorption time series are divided by the same BC time series),

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there is not necessarily any benefit to presenting results here as MAC as opposed to absolute absorption.

Figure 8: I do not understand the particular utility of this figure unless the authors are going to compare these calculations to their observations. It does not add any information that Fig. 9 does not already contain.

Fits: Are all of the linear fits shown in the manuscript one sided? If so, this is not appropriate since there is error in both the x and y axes. I recommend that the authors use a two-sided fit or use an ODR method.

P7128: A small  $R^2$  does not, by itself, indicate anything about the contribution of absorption by organic species. It may simply be an indication of measurement uncertainty. (Consider that I could theoretically do an experiment where I know that parameter x and y have a perfectly linear relationship, but my measurement methods are so noisy so as to hide this relationship. I am not saying this is the case here, only that low  $R^2$  values do not by themselves imply a fundamental lack of correlation.) However, since the authors do not show any correlation plots for wavelengths besides 870 nm (for which the best correlation coefficient is obtained), it is not possible for the readers to decide for themselves whether they agree with the presented interpretation or not. This is related to the broader issue of a lack of appropriate uncertainty analysis. I believe that scatter plots of absorption vs. [BC] should be shown for every wavelength as supplementary material.

The statement on P7128 that “the rather small increases in absorption for 870 and 532nm wavelengths at T1 compared to T0 suggests that the additional coating on the aged BC particles at T1 may not have produced an appreciable lensing effect” must be justified through rigorous consideration of absolute uncertainties involved in both the absorption and BC measurements.

In the abstract, the authors indicate that the MAC increases by  $\sim 60\%$  in going from T0 to T1. I do not believe that this is justified by the observations. They are, presumably,

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determining this by extrapolating the T0 results to shorter wavelengths and then comparing with the T1 results at 355 nm. This cannot be done because, as seems to be the case at T1, the absorption by brown carbon could take off below 375 nm at T0: the actual behavior is unconstrained and unknown. At best, the authors can compare the 405 nm MAC values between the two sites, from which they might conclude there was an increase of  $\sim 30\%$  between the two sites. However, any such comparison must also account for the absolute uncertainties in these measurements, which is not reported. A standard deviation here would not be appropriate, since that simply tells about the variance in the measurements.

On P7129, the authors state: “a more detailed analysis of the absorption data with the core-shell Mie theory, constrained with the observed BC coating thickness (from SP2 measurements) and morphological information (based on SEM images), is needed to estimate the relative contributions of the lensing effect”. I would urge caution here, because one can easily end up in a circular argument if SP2 LEO analysis is used to derive coating thicknesses since LEO analysis relies explicitly on core-shell assumptions and Mie theory. Thus, it cannot provide an independent measurement of coating thickness that can be used in Mie theory calculations.

P7126: As written, I find that the discussion of the Moffet and Prather work implies that their measurements were made concurrent with the measurements in this study. I suggest revising. Further, it should be clarified that Moffet and Prather did not observe an absorption enhancement of 1.6. The calculated this value based on Mie theory, constrained by their BC/coating ratio.

I am not certain I see the utility in the comparison between calculated scattering and observed scattering since loss of supermicron particles to the optical instruments is not well constrained. As they note: “the more than double overestimation of the scattering at 1064nm could have been caused by coarse mode particle loss in the inlet system

Minor comments

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P7117, L23: This is awkwardly stated. “85% of time. . .”)

P7119: I suggest “Since these PA instruments were designed” to measure both absorption and scattering. Really, in the context here, PA is a bit of a misnomer (or incomplete-nomer) since PA + photoacoustic and the scattering measurements are independent of the photoacoustic technique. Perhaps PA/RN (to indicate reciprocal nephelometer)?

Fig. 3 Caption: “particle mean diameter” should be “particle mean number-weighted diameter”

P7123, line 20 and throughout, as appropriate: I encourage the authors to use “larger than” or “greater than” as opposed to “enhanced” (larger is an adjective, enhanced is a verb)

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