Interactive comment on “Estimation of the mass absorption cross section of the organic carbon component of aerosols in the Mexico City Metropolitan Area (MCMA)” by J. C. Barnard et al.

Anonymous Referee #2

Received and published: 25 August 2008

General comments: This is an interesting paper following on the work by Kirchstetter et al. (2004) and Sun et al. (2007), made interesting by the use of ambient measurements.

However, I do have some concerns, particularly over the complicated (and potentially erroneous) way of measuring BC mass and H. How well does the H measured here - really an equivalent mixing height that accounts for aerosol absorption - reflect NO2 and SO2 vertical profiles?

Figure 4 also deserves further explanations, as does the exploration of how the calculation of H (which could have a bias - not uncertainty - when compared to the LIDAR
data) affects these results. I would recommend this paper for publication in ACP after the comments listed below are addressed by the authors.

Specific comments: Line 18: "high altitude of MCMA diminishes scattering by molecules" - gas molecules?

p. 10193: MAC of refractory OC is just 0.63 m²/g at 470 nm from Clarke et al., but the results from the current study apparently support that. So it appears Denkenberger’s theory may not be correct, or may not have a significant impact on the aerosol optical properties.

SR actinic fluxes to SSA using TUV4.4 model: but method used here is different. How is it different, and how does it change the errors in retrieved SSA compared to Goering et al. (shown in Table 2)?

How does g-lambda being at the upper end of previous reports affect the conclusions?

How does the AAE (Fig 1) compare with that at T2 - trend between 500-870 seems different, even flat between 500-673 nm? What does this say for the uncertainty associated with these measurements and the trends observed, including at the blue/UV range?

SO2/NO2 by DOAS - do you assume air is well-mixed throughout the mixing height? How are the gas concentrations converted to absorption? Was this wavelength-dependent?

The scaling height measurement uses BC mass and specific absorption; the authors assume a specific absorption and base BC on the Aethalometer’s optical measurement (and later note there are issues with this measurement). To me, it seems that the BC absorption (mass * specific absorption) could have been determined from the Aethalometer (for the specific wavelength), without relying on either the Aethalometer’s calibration or the Barnard et al. (2007) estimate for specific absorption. Have the authors considered this possibility?
Still, the authors suggest that the mixing height is fairly steady depending on the time of day. If this is indeed the case, then one might think the use of H from the lidar measurements at the end of the month would be much simpler and just as accurate without the uncertainties induced by the Aethalometer and the measurement of specific absorption.

On the other hand, the study hinges on H, better-defined (as I understand it) as the equivalent (not actual) mixing height corresponding to the columnar absorption by BC, because it is not essential that the columnar aerosol loading follow a plug profile (e.g. there could be pollution layers above the PBL), and yet, given just the surface measurements, that is what is assumed in this paper. So the use of actual H-values might be more appropriate to the results obtained here. Or am I missing something here?

Table 1, AAE: Why are there 3 values of AAE given only two wavelength ranges, 300-500 nm and 300-870 nm, in the table header? And why are the AAE values so different (e.g. 1.55, 4.5, 2.8 for April 12 case) over these ranges?

Eq. 4, p. 10202: The AAE apparently uses measurements at 415 nm and 500 nm to determine the AAE; so it seems obvious that the extrapolation using the 500 nm extinction coefficient should match with measurements. The only validation appears to be the 368nm measurement, on which rests the "matches extremely well" qualification of the extrapolation. So I am not sure the extrapolation further to 300 nm is necessarily valid (or well-validated). Comment?

The term lambda-o is not explained, though I assume this means 870 nm, the reference for Cbc? How well does the inverse wavelength dependence (AAE = 1 for BC) describe the behavior at wavelengths below 500 nm, which is where all of the organic absorption takes place? This is not explained by the authors.

p. 10204: I do not understand the point of the paragraph starting at line 2 about dust absorption at T2. That site is not considered in this study, so...?
Figure 4 and related text: (1) Are the MACs based on OC mass or OA mass? The AMS measures OA mass, so unless you used an OA/OC ratio (that is not specified), this term may be incorrect. (2) The MAC of OC/OA drops to almost zero between 400-500 nm - this rules out an unknown absorber, because all absorption is accounted for by BC and/or dust. So there has to be some other reason - an overcorrection for NO2, or even BC, perhaps (though it appears you eliminated the NO2 possibility). Comment? (3) Also, I thought NO2 was based on the DOAS data, so how is this concentration "assumed" as stated on line 7 of p. 10205? Further, do you know that the concentrations are the same over the entire column (see comment on NO2/SO2 measurements earlier)? (4) The striking knee around 400 nm is not seen in the April 18 data. Comment?

Regarding the discussion of "error" in H, the comparison with the lidar data suggests a bias of 10-20%, not an uncertainty. If you used the lidar H values, would you get different MACs, particularly between 400-500 nm?

It might be interesting to see a plot of spectral irradiance, with corresponding values for BC, OA and dust absorption.

Interactive comment on Atmos. Chem. Phys. Discuss., 8, 10189, 2008.