**Atmospheric
Chemistry
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Discussions**

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.

J. C. Barnard et al.

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We appreciate the reviewer's very thorough review!

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?

[reply] Without knowledge of the vertical profiles of SO2 and NO2, we can't say for certain if the equivalent mixing height for aerosols, H, is the proper mixing height for

the gases SO2 and NO2. All we can do is examine the effect of the uncertainties in the inferred columnar absorptions of these gases on the MAC values. This is done for NO2 in section 3.2 of the original paper. The SO2 absorption if confined to wavelengths around 300 nm and is very small, and uncertainties in the SO2 absorption make little difference in the computed MAC values.

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?

[reply] Yes, we are taking about molecular (Rayleigh) scattering. In the revised text, we added "gas" in front of 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.

[reply] It's difficult to know to what extent Denkenberger's theory influences the optical properties measurements in Clarke et al.'s work. We suppose that it's worth mentioning the possibility that heating during aerosol measurements may alter their optical properties in the manner described by Denkenberger et al. We note, as does the reviewer, that our results lend some support to those of Clarke et al., that is, the MAC is small (less than one) around 470 nm. However, we are cautious about drawing conclusions regarding the exact magnitude of the MAC around this wavelength because the error bars on our results are fairly large. If Denkenberger's theory reduced the MAC from, for example, 1 m^2/g to 0.5 m^2/g at 470 nm, our results could not be used confirm this change because the change is smaller than the error bars (explained in section 3.2)

We added some text in section 1, to show that we really don't know whether Denkenberger's theory applies to Clarke et al.'s work:

"However, it is difficult to assess quantitatively to what extent, if any, the mechanism proposed by Denkenberger et al. influences the results of Clarke et al."

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)?

[reply] We have covered this issue in responding to reviewer 1 comments. We repeat here the revised text in section 2.1:

"The actinic fluxes from the SR were inverted to find SSA using a different method, based on the TUV4.4 model. Goering et al. (2005) and Michalsky and Kiedron (2008) describe the use of this model applied to surface irradiance measurements to find SSA from either UV-MFRSR measurements or Rotating Shadowband Spectrometer measurements. The method we employ here is slightly different than theirs because we use the TUV4.4 with actinic flux, not irradiance, to find SSA. To compare the Kassianov et al. and TUV4.4 methods, we applied the TUV4.4 methodology to the MFRSR irradiance data to infer SSA and then compared these values to those obtained from the technique of Kassianov et al. (2007). The largest difference was 0.02, although typical differences are 0.01 or less."

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

[reply] This is a very good point because there is a direct relationship between g-lambda and retrieved SSA values. In particular, smaller g-lambda values are associated with larger retrieved SSA values. That being said, using the retrieval method of Kassianov et al., the retrieved SSA and g values are derived from the retrieved size distribution, using the same refractive indices, are therefore consistent with one another. But the Kassianov et al. method is applied only to the MFRSR wavelengths (415 nm

is the lowest wavelength) and extrapolation, explained in the text, is used to find the g values at lower wavelengths. If these extrapolated g-values are too large, then the SSA values will be biased to low. We have added text to indicate this in section 2.1:

"This value is at the upper end of the range of g-lambda values reported by Wenny et al. (1998) for 312 nm, suggesting the possibility that the extrapolated values are too large. If the values are indeed too large, then the retrieved SSA values will be too small. For example, sensitivity tests using the TUV4.4 model show that, if we assume that g-lambda equals 0.76, then the retrieved SSA value is 0.70 at 300 nm. But if we change g-lambdavto 0.66 – a rather substantial amount – then the retrieved SSA value rises modestly to 0.725, still within the uncertainty of SSA stated above."

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?

[reply] The AAE for T2 (for this particular day) does not quite follow the 1/lambda law. What this says is, yes, that there are uncertainties in the SSA inferences, and/or a failure of strict adherence to the 1/lambda rule. And yes, this implies that the 1/lambda rule may not be strictly followed in the blue/UV range for BC. However, as noted in the responses for reviewer #1 above, there's a fair amount of evidence that the 1/lambda rule is approximately followed.

To get to the bottom of this issue would require that we fully analyze the data at the T2 site – an activity that is beyond the scope of this paper. The reason we present this case is to show that the decrease in SSA at lower wavelength is not necessarily confined to the urban MCMA area. When faced with the choice of showing this figure or not showing this figure, we decided to show it, because the results are interesting and support that case that the roll-off of SSA at lower wavelengths also occurs at a rural site. But whether the decrease observed at T2 is caused by the same phenomena

acting at the urban site remains to be seen. We have changed Fig. 2 by adding a "1/lambda" line, as well as the plus or minus 0.03 error bars to the single scattering albedo. The text at the end of section 2.1 has been considerably altered:

"This figure also shows by the black line the extrapolation of SSA at 870 nm to lower wavelengths, assuming that the absorption follows the lambdaˆ-1 rule. For this site, adherence to this rule is less evident than shown in Fig. 1. This lack of adherence cannot be solely attributed to a failure of the lambdaˆ-1 rule, because the rule may be followed but is masked by uncertainties in SSA. Recall that this uncertainty is about +-0.03. At 500 nm, the lambdaˆ-1 relationship lies just outside the top of the error bar. Of course, had we chosen to extrapolate the lambdaˆ-1 relationship from the SSA at 670 nm, the line would lie within all error bars above 500 nm. That the SSA at 415 nm is lower than the SSA at larger wavelengths is similar to the behavior seen in Mexico City. Without further analysis of the T2 data, beyond the scope of this paper, we cannot be certain that this behavior is caused by the same factors acting at the Mexico City site, such as aerosol composition and size distribution."

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?

[reply] Yes, we assume that the gases are well-mixed throughout the depth of the atmosphere up to the mixing height. The gas concentration is converted to columnar absorption by multiplying the columnar gas abundance by the absorption coefficient. It is obviously necessary to consider the wavelength variation of the absorption, and this variation is accounted for in our calculations. Here's some text to indicate what we've done, in section 2.2:

"For these corrections, the gases were assumed to be well mixed from the surface up to the height H, and from this assumption we determined the columnar abundance of gas. The columnar absorption is calculated as the columnar abundance multiplied by

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the appropriate absorption coefficient, a function of wavelength."

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?

[reply] Yes, the absorption can be obtained from aethalometer data (see Arnott et al., 2005, Aerosol Science and Technology, 39(1)). This is a big job, however, and subject to its own uncertainties, and we think it is far outside the scope of the paper. We opine that it is unlikely that uncertainties in the results would be improved significantly by using the aethalometer absorption directly.

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.

[reply] The real issue here is uncertainties. We are trying to balance the uncertainties of the "aethalometer/specific absorption" determination of H against the uncertainties of the using the "lidar" method. As noted by the reviewer, the lidar mixing height inferences are made more problematic because they were made during the end of April 2003, while all our case studies are from the beginning of the month. So what's the best choice? We can't tell.

Therefore, the best way around this problem is to simply state in the revised paper that had the lidar mixing heights been used to calculate the MAC, the MAC values would be different by about 20%. We cannot beat down the uncertainty lower than this! This

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has been acknowledged fully in the section that describes uncertainties. We add a little more text to underscore this point, at the end of section 2.3:

"Given the difficulties in determining H, this level of agreement seems satisfactory, but it must also be recognized that the uncertainties in H, around 20%, is a floor to the overall uncertainty of the MAC values derived here."

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? Comment?

[reply] Hmmm ... we don't quite understand the point that the reviewer is trying to make. It is not necessary to assume a plug profile of gas. The most common notion of a scale height for a gas (or other substance) assumes an exponential decrease with height (See Goody, Principles of Atmospheric Physics and Chemistry, Oxford University Press, 1999, page 10.), so that $c(z) = CoExp(-z/H)$, where Co is the surface concentration The total columnar concentration is therefore Co*H, the same as one gets assuming a plug profile. We appreciate the reviewer's question, but we don't know if we are answering the question adequately because we don't quite understand the question. Because we cannot know the exact scale height, we are forced to estimate it, and uncertainties in the scale height become the important issue. This issue has been examined in section 3.2.

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?

[reply] We realize that the AAE values listed in Table 1 have caused a lot of confusion.

To make these values clear, we have made a separate table to list them. This is the new "Table 2". Note that the confusion caused by the original table has caused this reviewer to interpret the three values listed in old Table 1 as AAEs, when in fact, one value is the extinction Angstrom exponent (1.55), while the other two values are AAEs over the wavelength ranges indicated above.

We disagree with the reviewer who states that the AAE values for April 12 are significantly different than the other days. Have a look at the new Table 2. (Maybe the reviewer's observation stems from confusion regarding the original Table 1).

To explicitly note the wavelength range over which the Angstrom exponent was calculated, we add the text in Sect. 2.1:

" ...as well as the Ångström exponent determined between the wavelengths of 415 nm and 870 nm." This range is also explicitly labeled in Table 1.

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?

[reply] The reviewer apparently missed something here, because it says right in the text, immediately below Eq. 4, that the Angstrom exponent is derived from the 415 and 870 nm channels of the MFRSR. Also, the Angstrom exponent is not an AAE (absorption Angstrom exponent), but rather a traditional (extinction) Angstrom exponent. We think this distinction is clear in the existing text. The fact that the extrapolation from 500 nm to the data point at 368 nm is very good, suggests that the extrapolation to 300 nm might also be good. But we will "tone things down" in the revised text, section 2.4:

" ... indicate that the Ångström relationship is satisfied well between the wavelengths

of 368 nm and 870 nm. This in turn suggests that the extrapolation of the extinction to 300 nm will be reasonably good, although optical thickness measurements at 300 nm would be necessary to confirm this assertion."

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.

[reply] The reviewer must be referring to Eq. 5 ?

We have made clear the definition of lambda-o in the revised text, immediately under Eq. 5:

"The notation lambda-0 (= 500nm) means that lambda-0 is set equal to 500 nm."

Reviewer #1 is also concerned about the issue of the inverse wavelength relationship, and we have responded to this issue above (under reviewer 1). Note the Bergstrom et al. (2002) state that the "data show an approximate 1/lambda variation between 0.4 and 1.0 microns", – the wavelength range of their data. The data of Kirchstetter et al., 2004, show that the 1/lambda relationship seems to be well satisfied down to 330 nm (see Figure 1 in Kirchsetter et al.), for "motor vehicle" aerosols, in which BC is the primary absorber.

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...?

[reply] The point of showing this figure is that the SSA tends to decrease as the wavelength decreases at another, rural site near the MCMA. We mention the issue of dust, because during the MILAGRO campaign, there was a lot of dust at the rural T2 site. Because dust is a notorious absorber in the near-UV and UV, as stated in our paper, it could cause an SSA roll-off with decreasing wavelength as seen in Figure 2. But the fact that this SSA behavior was seen after rainfall, which would scavenge the dust

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from the atmosphere, implies that the roll-off of SSA at the lower wavelengths cannot be attributed to dust. We think these issues have been made very clear in the existing text. We state explicitly in the text that " ... it is unlikely that the SSA behavior seen at T2 on this day can be attributed to dust". The preceding paragraph gives a description of dust absorption so that the reader should be prepared for this statement.

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?

[reply] Taking these 4 points in turn:

(1) The reviewer makes a good point. It is important to distinguish between OC and OA mass. In the paper we are referring to OA mass, and we have taken steps to make this clear. Early in the manuscript, section 2, we state "We also note here the distinction between OC and OA mass, as described for example in Turpin and Lim (2001), where OC mass is the measured mass of carbon molecules associated with organic compounds, while OA is the mass of these compounds." We have also changed the abbreviation "OC" to "OA" when appropriate, and the abbreviation "OA" is now used in the abstract.

(2) It's difficult to pinpoint which factors contribute to the negative MAC at around 500 nm. We cannot say that it is the 1/lambda assumption, or the inferred NO2 concentra-

tion, or ??. We have shown in the paper that an error of 1 DU in NO2 concentration can turn negative MAC values into positive values at 500 nm. Also, in the text we noted that the random and systematic errors are relatively large and may contribute to the negative MAC values at 500 nm. To make this more explicit, we have added this text at the end of section 3.2:

"The magnitude of the random and systematic error at 500 nm may account for the negative MAC values as observed for some of the cases studies shown in Fig. 4."

(3) Here we appreciate the reviewer's good eye. We changed "assumed" to "inferred".

(4) Hmm ... We cannot explain the absence of the striking knee for April 18th. That's a good observation by the reviewer. The inferred columnar NO2 concentration on that date is lower, but not that much lower, than the other case studies so it is unlikely that NO2 concentrations explain the absence of this knee.

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?

[reply] From Eq. 3, we see that MAC is proportional to 1/H. So substituting the "lidar" H values for the "aethalometer" H values would not in itself change negative MAC values to positive ones. However, using the lower lidar H values would reduce the inferred columnar absorption by NO2 by about 20%, which would tend to increase the MAC values in the spectral region where NO2 absorbs. We already have noted in the original paper, section 3.2, that reducing the NO2 concentration (or equivalently, the columnar absorption) by 1 DU, increases the MAC value at 500 nm by 0.5 m^2/g. At 415 nm, this increase is 1.3 m^2/g. A change in NO2 of 1 DU is about a 50% change from the inferred values. Assuming the change in MAC is linearly proportional to the change in NO2, the 20% change in NO2 would correspond to changes of +0.2 m^2/g and +0.5 m^2/g at 415 nm.

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

[reply] This request is a little vague, and we don't understand exactly what reviewer wants: The atmospheric columnar absorbance, in watts/mˆ2, for each of these constituents, as a function of wavelength? This would be an interesting graph, but could only be constructed theoretically using a radiative transfer model. We are not sure that would add much to the paper because we think this information (except for dust) is contained in (new) Table 4, although in this Table the irradiances are integrated over the shortwave spectrum. Because we have shown that dust absorption is expected to be very small, there's not much point in adding a dust component to this Table. For example, from looking at this table, one finds the absorption of the BC component of the aerosol by subtracting row 1 from row 3. To find the absorption by OA, subtract row 3 from row 2.

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