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Interactive comment on “Measurements of Black Carbon Specific Absorption in the Mexico City Metropolitan Area during the MCMA 2003 Field Campaign” *by* J. C. Barnard et al.

J. C. Barnard et al.

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I am pleased to respond to the reviewer comments. My responses are provided below. I have numbered my responses so that they can be referred to by number as necessary. The paper has been extensively revised, with some reorganization. The largest change is the presentation of the results first, followed by a lengthy section (2.5) that discusses the uncertainties associated with each method. Because of space limitations, I cannot provide the reviewers original comments here.

Anonymous Referee #3 1) It’s a good idea to try to improve the estimation of the aerosol burden by a more detailed look at the LIDAR returns, but in this case it is not possible without a lot more work, outside the scope of the paper. And good results would not be guaranteed. The raw lidar returns are backscatter. Scaling raw backscatter to the surface values is not too useful because backscatter is only crudely proportional to aerosol abundance. To convert these returns to something more useful for determining aerosol abundance – aerosol extinction – is a fairly difficult task fraught with uncertainty. This difficulty has recently been shown, for example, in comparisons of lidar-derived vertical extinction profiles with profiles obtained from an airborne sun photometer. (These results have not yet been formally published). With this in mind, we do not think we can reliably derive the aerosol extinction profiles that would lead to a better estimation of the aerosol burden. However, the LIDAR profiles of backscatter and depolarization ratio have been very useful in determining the top of the aerosol mixed layer.

2) We cannot estimate with exactness the uncertainty of method I. However, the available evidence suggests that the specific absorption values obtained from this method are probably close to being a lower bound on this quantity. The evidence is based on the following: a. the use of the surface concentration as an index of the concentration throughout the entire mixed layer probably overestimates the BC burden (because concentration would tend to drop with height consistent with gradient transport theories of fluid transport). This idea was mentioned in the original manuscript. b. The aethalometer may be overestimating the BC concentrations. In this regard, we have added in the revised manuscript (sec 2.5.1) a more comprehensive assessment of the aethalometer performance. Using the empirical correlation between carbon monoxide and thermally determined elemental carbon (EC) developed by Baumgartner et al. (2002), it appears that the BC concentrations registered by the aethalometer are sometimes biased too large (at least when compared with these proxy EC values). These two factors (a,b) working together suggest that method I overestimates the columnar mass of BC in the atmosphere, and therefore underestimates the specific absorption. We have mentioned this tendency for underestimation many times in the revised manuscript, including the abstract. We cannot hope to specify the uncertainty with greater precision, but the “lower bound” conclusion is nonetheless useful.

3) This is a good point. In the revised manuscript, we have clarified our choice of density (end of Sec. 2.2 and Sec. 2.5.2). Plausible ranges for BC density range from 1.7 to 2.1 g/mˆ3, however, there is no reason that the particular value 2.0 g/mˆ3 is appropriate for this site, so we merely chose this value for convenience in comparing our results to Schuster et al. (2005). We have added a section (sec 2.5.2) about uncertainties in the inference of the specific absorption, which includes a brief discussion of the uncertainties due to the choice of density. We estimate the worst case uncertainty of method II to be about +/-40%, and this is mentioned in the abstract.

4) Sec. 2.5.2 estimates the uncertainty in the imprecise knowledge of the refractive index to be about 22%. (i.e., the change in specific absorption if the refractive index used in the calculations was 1.75 - 0.7i [certainly a plausible value] instead of 2.0 - 1i). We have simply tried to put bounds on the calculation of the specific absorption using reasonable values of the refractive index that span a range of plausible values. We note in passing in the revised text, that using the OPAC refractive index, 1.75 - 0.44i, lowers the calculated specific absorptions considerably, but recent evidence presented by Bond and Bergstrom (2004) suggest that the OPAC refractive index is not dark enough.

5) To address the uncertainty issue, we have added a Sec. 2.5. This section amplifies the discussion of uncertainties found in Schuster et al. (2005). In this section we have considered other factors such as the non-spherical shape of the particles and contamination by other absorbers.

Other specific comments: 6) Changed to “another method”

7) For method II, we estimate the worst case uncertainty at +/- 40% (noted in the abstract and the conclusions). This translates into an uncertainty of about +/- 3.6 mˆ2/g, mentioned in the revised manuscript. Although this uncertainty is large, it is much less than the reported variability in the specific absorption (2 to 25 mˆ2/g). For the MCMA, the only way to achieve a specific absorption of say, 13 mˆ2/g, would be to

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use a rather dubious combination of soot density and refractive indices. This, too, has been noted in the conclusions.

8) The revised manuscript has addressed this issue at the end of first paragraph, Sec. 2.1.

9) The lidar backscatter does indeed show sharp gradients at the top of the aerosol mixing layer. The presence of aerosols can also be detected by looking at the lidar depolarization ratio, which tends to be large when aerosols are present and much smaller when only air molecules are present. For identifying the top of the mixed layer, the depolarization method was used because the gradients are sharp. I do not know if this identification was done automatically, or whether it was done by eye. I have been trying to contact my co-author who knows this, but he has returned to Germany (by sailboat) and I haven't been able to communicate with him for several months. Use of the depolarization ratio is mentioned in the revised paper in Sec. 2.1. By looking at the few profiles of depolarization ratio I have on hand, it appears that the ambiguity in identifying the top of the mixed layer is about +/- 15%. The issue discussed here is a minor issue and will not affect the conclusions presented in the paper.

10) OK, this change has been made.

11) Yes, I agree this is confusing (as did most of the reviewers!). I have simplified this section by deleting the reference to Moosmuller and adding an additional reference by Bergstrom et al. See revised manuscript, Sec. 2.3:

12) Fuller et al. show in Table 7, and in Figures 13 and 15, that over plausible ranges of BC mass mixing ratios (about 0 to 0.20), and various mixing schemes (Table 7), the specific absorption remains less than 10, unless the particles become large. These calculations are done for a dry aerosol consisting of BC mixed with ammonium sulfate. The mass mixing ratio for the Mexico City aerosols can be inferred from f_v and reasonable assumptions about the densities of the shell and core. The BC mass mixing ratios so estimated clearly fall within the range demarcated by Fuller et al. There's

some reworded text that I hope clears the air in Sec. 2.3.

13) Yes! Larger amounts of BC mean smaller omega. Seems to makes sense. I didn't mention this in the revised manuscript because I thought the mention of 18 April was sufficient.

14) Thank you for the idea of casting the results of method I in terms of a lower bound. This idea is now emphasized in the revised manuscript (i.e., see point #2 above). The prose "removing these values from consideration" has been deleted from the revised manuscript.

15) The winds that advect the aerosols over the AERONET site blow towards the southwest and towards a large mountain ridge. Therefore some recirculation over the AERONET site might be expected. This has been mentioned in the revised manuscript.

16) Other reviewers requested that we calculate the specific absorption using AERONET aerosol volume retrievals for the days in question, rather than using "climatological" retrievals. We have complied with this request. The newly calculated specific absorptions are slight different that the "climatological" ones, but the derived real part of the shell refractive index has changed from 1.56 to 1.39. We found that the real part of the AERONET retrieved refractive index is 1.40, when averaged over the days of our study. We mention these two values (1.39 and 1.40) in the revised manuscript, Sec 2.3. We did not cite a percentage difference because these values are obviously very close.

17) I have read AERONET papers where it is mentioned that measurements are made at 500 nm by the AERONET sun photometer. Therefore I assume that the AERONET sun photometer in Mexico City makes a measurement at this wavelength and no extrapolation is necessary.

Technical Comments: These have been taken care of.

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18) Our derived values of specific absorption at 550 nm are 6.8 mˆ2/g and 8.1 mˆ2/g. In the paper, I have mentioned he specific absorption, 9.5 mˆ2/g @ 550 nm, found by Schuster et al. (2005). Like our methodology, Schuster et al. relies solely on optical means to find the specific absorption. Using optical means to measure absorption, and thermal means to determine elemental carbon (EC) mass, Baumgartner et al. (2002) found that at the surface, the specific absorption was 7.0 mˆ2/g at 550 nm. These results cluster in a range of about 7 to 10 mˆ2/g @ 550 nm. These findings was been stated in the abstract and conclusions of the revised paper.

19) An entire section has been added to the paper regarding the uncertainties, Sec. 2.5. Additionally, we have expanded the discussion of the aethalometer measurements, sec. 2.5.1, and noted that even thermal EC measurements are problematic (by citing the “round robin” tests described by Schmid et al. (2001)). The uncertainties associated with method I are so large, that we cast the specific absorption values obtained from this method as lower bounds to the true specific absorption. For method II, the “worst case” uncertainty appears to be about +/- 40%. This has been stated in the abstract and the conclusions.

20) All we have to work with is the lidar backscatter and lidar depolarization. These measures can sense the presence of aerosols, but cannot be used to tell how much aerosol is present. These data are best used to find the top of the aerosol mixed layer. See point #9 above.

21) We have greatly expanded the discussion regarding the aethalometer. By comparing the aethalometer measurements by proxy EC measurements obtained using the method of Baumgartner et al. (2002), and specifically tuned to Mexico City, we concluded that the aethalometer in MC has a tendency to register BC values that are too high (mentioned in new Sec. 2.5.1) This finding, and the issues regarding the distribution of aerosols in the convective boundary layer, suggests that columnar mass estimates from the aethalometer/lidar combination are close to being upper bounds, and therefore the specific absorption derived from this method is close to being a lower

bound.

22) After further discussion with the aethalometer's mentors, I realized that the aethelometer was run in “tape saving mode”. In this mode, the tape is not exposed to the aerosol air stream during the entire measurement cycle; at times some of the flow is diverted past the tape. This mode is fully discussed in the aethalometer manual (www.mageesci.com). The text has been changed to reflect this new understanding (Sec. 2.5.1).

23) Some text has been added to the revised paper. Of course, as the reviewer notes, this argument is far from perfect. Here's the text: The assumption required by method I - that BC does not exist above the aerosol mixed layer - can be made more credible by considering a two layer atmosphere: one layer consisting of the boundary layer that develops during the day and the residual layer above the boundary layer. The residual layer may or may not contain aerosols transported upwards by the previous days' boundary layers. If the residual layer is clean, that is, if it contains background aerosols with little BC, then the light absorption will be confined to the boundary layer, laden with the emissions of the day. Then the strong correlation exhibited in Fig. 3 is expected. If on the other hand, if the residual layer contains a significant amount of BC then the correlation seen in Fig. 3 would be much weakened. Realizing that this argument is far from perfect, we conjecture that little BC exists above the mixed layer.

24) Much has been done. We have added a whole new section on the uncertainties associated with method II, sec 2.5.2 We discuss uncertainties stemming from a) unknown density of BC, b) unknown optical properties of BC, c) mixing assumptions and aerosol shape, d) contamination of the results by other species, e) uncertainties in the AERONET volume distributions. These uncertainties, when simply summed together (a procedure that does not allow error canceling) amount to about +/- 40%.

25) In regards to the empirical parameterization - we abandoned this approach and now use AERONET volume retrievals for the day in question (as requested by other

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reviewers). This new approach only changes the average specific absorption value slightly, for 9.2 mˆ2/g to 8.9 mˆ/g; however, the real part of the shell refractive index changes a lot (see point #16 above).

26) The words “more rigorous” and “less approximate” have been removed.

27) We have in the revised paper, both in the abstract and conclusions, noted that the method I results probably represent a lower bound on the specific absorption values. I think that the pros and cons of each method are clearly spelled out in the text and need not be summarized, which would increase the length of an already lengthy paper.

We have added Baumgartner et al.’s (2002) finding that the specific absorption is 7.0 mˆ2/g at 550 nm, determined using a PSAP (to find absorption) and thermal methods to find the EC responsible for this absorption.

28) The fit curve has been removed from this figure.

29) OK. We revised the following text in the conclusions: When averaged over 7 clear periods of the MCMA-2003 field campaign, consisting of a total of about 10 hours in the morning time over the month of April 2003, the values of the specific absorption are 7.5 mˆ2/g and 8.9 mˆ2/g, for methods I and II, respectively, at 500 nm.

30) The uncertainties of both methods are now emphasized in the conclusions as well as the abstract (see point #24).

Minor Comments: 31) We agree. We request that the title will stay as is. The word “effective” is now mentioned in the abstract.

32) These keys words have been added to the abstract. Good idea!

33) Done. See revised text in Sect. 2.1.

34) This issue is not so relevant for the aethalometer data. One can take the aerosol number distribution derived from the AERONET volume distribution, dn(r)/dr, multiply by the absorption efficiency, Q(r,lambda=500 nm), for a coated aerosol with a BC core,

and multiply again by the geometric cross section, Pi*rˆ2. This gives the absorption as a function of particle size (units: metersˆ-2). Integration gives the absorption coefficient at a particular wavelength (units: metersˆ-1). We find that the large particles contribute negligibly to the absorption and scattering. (Their absorption cross sections are large, but there are too few of them to matter). So we do not need to be concerned about line losses for the big particles because the amount of scattering and absorption they contribute is very small.

35) Done.

36) The top of the boundary layer, as found from the potential temperature profiles, was estimated by eye. The top of the aerosol mixed layer may have been found by eye (but I am not sure because I cannot find my lidar colleague who left the USA and went back to Germany on a sail boat). I am leaving the prose unchanged except to mention that the top of the boundary layer was found through a visual examination of the potential temperature profiles.

37) This point has been brought out in the expanded discussion about the aethalometer; to wit: For the sampling period, all of the seven channels were found to be in excellent agreement, with a variation from 1-2%, indicating that black carbon was indeed the major light absorbing material present in the aerosol, if not the only one. This conclusion assumes, of course, that the wavelength dependence of the BC aerosols exhibits a lambdaˆ-1 dependence, which is strictly speaking is only true the small particle limit (Bohren and Huffman, 1983), but has been observed in atmospheric aerosols (Bergstrom et al., 2002).

38) “Collapse” is common terminology in the world of fluid mechanics that would describe the physical changes in the MC boundary layer in the late afternoon and evening, brought on by increasing atmospheric stability (among other things). Because most readers may not be aware of this terminology, I have changed the word “collapse” to “decreases”.

39) This is a good point and has been taken care of in the text.

40) This section confused almost everybody and has been revised. See point #11 above.

41) We have briefly discussed the possibility of the effect of OC absorption in the "uncertainties" section 2.5.2. This discussion is found under the heading of "Contamination of results by other absorbing species". Making retrievals at 500 nm helps reduce unwanted contamination by dust, OC, and NO2, because these substances generally absorb significantly only at lower wavelengths.

42) This section has been completely revised, and the comparison between our results and those of Schuster has been shortened. The conclusions follow where we provide summarizing remarks regarding the comparison of all the results.

43) We changed our wayward ways and no longer use the parameterization of Dubovik. Instead, we now use the daily AERONET volume retrievals for the days in question. See point #25 above.

44) Done.

T. Bond (Referee) yark@uiuc.edu 1. Overall comment 45) I think the assertion that "specific absorption does not appear in this work" is a matter of opinion, and my opinion is different than the reviewer's. Let's say that we have a nearly complete knowledge of the aerosols including their shapes, their compositions, the refractive index of each component of the aerosol, the vertical aerosol distribution, usw. Let's assume that, given this information, we can compute the aerosol optical properties with little error. Then – in principle – we should be able to find the specific absorption with small error, and that's because the physics of the radiative transfer problem is known. So in my view, calculating the specific absorption from optical methods is not a problem in developing new physics, but rather it's a problem of having accurate input to the problem. In other words, there's no fundamental reason why the specific absorption cannot be found using optical methods, but there are certainly very formidable practical challenges. I fully admit that we don't have "well known" inputs and therefore the inferences of the specific absorption published here are subject to large uncertainties (as are almost all determinations of the specific absorption in the atmosphere). I have added an uncertainty section, Sec. 2.5, which shows that the uncertainties surrounding the methods described in our paper are indeed large. When considering these large uncertainties, one must keep in mind the large uncertainties associated with other methods. For example, Schmid et al. (2001) shows that there are large differences in determining EC from various thermal/optical methods, and ways of finding the specific absorption that rely on these methods would be subject to large potential errors.

46) I confess that I'm not the "sharpest tool in the box", but I don't understand this reasoning at all. I readily admit that the determination of the columnar mass of BC is fixed by the procedure AND with the specification of the density. The columnar mass of BC must be related to the single scattering albedo (under the assumption that BC is the only atmospheric absorber). I don't see a problem. However, the results would be much more certain if it were possible to make an independent measurement of the columnar mass of EC, but at the present time, such a measurement appears impossible. I would like to know what requirements are necessary for a measurement and/or inference of specific absorption to be "valid".

47) Professor Bond is certainly correct that the aethalometer has a lot of problems. I have added a new text that discusses these issues, see point #21 above.

Continuing on, let me attempt to rephrase her argument. Assume a hypothetical aethalometer calibration coefficient that can somehow change to account for changes in the specific absorption of BC deposited on the aethalometer tape. Then for a given amount of measured attenuation, the mass of BC derived from the aethalometer could vary, because of changes of the specific absorption of deposited BC. Applying our hypothetical calibration coefficient(s) to the aethalometer attenuation data would result in BC mass determinations that would be nearly perfect (aside from line loss issues, etc).

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Now let us further assume that the measured surface BC concentration is an excellent index for the concentration of BC throughout the mixed layer, and by application of Eqn. 2 in the paper, MBC can be found almost perfectly.

It would still be possible for the specific absorption to change using method I, through changes in the measured single scattering albedo, which would change is response to changes in the specific absorption (even with a fixed amount of BC mass). This conclusion is contrary to what the reviewer has stated above, so I suppose I don't quite understand her argument.

I have noted in the conclusion that:

At the present time, the results are can be considered "radiatively correct", meaning that given the assumptions made, the alpha values are consistent with two measured optical properties of the atmosphere (tau, and omega_naught) and the irradiance field at 500 nm.

I have also noted in the conclusion that to obtain large values of the specific absorption (greater than about 12 mˆ/g), one would have to assume rather dubious values for the optical and physical properties of BC.

2. Specific comments 48) I have added text to clarify this issue, see point #8.

49) The text has been changed to note that the refractive index is relatively constant in the visible region.

50) See point #23. Also, I have changed some of the text to read, for example: and the unique meteorology of the Mexico City basin, which under the right meteorological conditions, may flush pollutants out of the basin on a daily basis (Molina et al., 2002; Whiteman et al., 2000; Gaffney et al., 1999; Fast and Zhong, 1998).

51) Professor Bond is again correct that other atmospheric absorbers exist including dust and organic carbon. These substances tend to absorb in the UV and near-UV. The selection of a wavelength of 500 nm tends to avoid the problem of dust and OC

absorption; however, some absorption may occur, and this is an uncertainty that is guessed at in our uncertainty analysis. (We have to resort to some guessing because it is almost impossible to precisely determine the possible absorption of organics at 500 nm).

52) Unfortunately, no, because we have not made much progress in converting the RAMAN nighttime data to extinction. And even if extinction is known during the night, it is difficult to extrapolate these profiles to daytime conditions because of changing relative humidity, and the change in the boundary layer structure. (We had long discussions about exactly this issue and decided we couldn't do it reliably).

53) Instead of using climatologically-based retrievals, day specific retrievals are now used. See point #16.

54) This text confused the other reviewers and has been rewritten, see point #11.

D. Baumgardner darrel@servidor.unam.mx 1)The title of this manuscript should be changed to “Derivations of Black Carbon Specific Absorptions etc.”. The specific absorptions are not being measured, as advertised in the title. 55) I wish the title to remain the same, as endorsed by reviewer O. Schmid, who states: In response to one of D. Baumgardner's concerns and provided the term ’effective’ is introduced (see introductory comment) I do not object against the word ‘Measurements’ in the title, since it is common practice to also refer to indirect methodsas measurement methods.

56) This is admittedly an oversight on our part. We found Dr. Baumgardner's papers to be very useful. These papers are now discussed in the revised text, including the abstract and conclusions. It proved to particularly useful to have an independent measure of the (surface) specific absorption (Baumgardner et al., 2002), surface measurements from which one could derive the single scattering albedo (Baumgardner et al., 2000), and a method of converting carbon monoxide measurements to EC (Baumgartner et al., 2002).

57) If I understand this comment correctly, Dr. Baumgartner is asking why the aethalometer uses a specific absorption value of 19 mˆ2/g, yet our inferred specific absorptions are less. It is well-known that embedding absorbing particles in a filter matrix enhances their absorption due to multiple scattering. This has been mentioned many times in the literature (Petzold et al., 1997; Arnott et al., 2005). Thus, the calibration coefficient can be larger than the actual specific absorption of the ambient aerosol.

We agree with Dr. Baumgartner that the aethalometer measurements are uncertain, and we have now discussed this uncertainty in some detail in the revised manuscript (see point #58 and #2).

58) The above study has proved to be useful. Not only does the measured value quoted above (7 mˆ2/g) fall into the range of values bracketed by our study, the use of Dr. Baumgartner's proxy elemental carbon (EC) method (i.e., inferring EC concentrations from CO measurements) have suggested that the MC aethalometer is reading somewhat too high (compared to these proxy EC measurements). These points have been mentioned in the revised manuscript.

59) The reviewer assumes that we didn't look at the lidar profiles. We did. The aerosols seem amazing well mixed when the boundary layer is fully developed. Even some of our lidar experts were taken aback at the smoothness of the backscatter profiles that indicates a lack of aerosol layering.

60) Opinions differ on this subject. It is true that the circulation in MC basin is very complex, but modeling studies constrained by meteorological observations (Fast and Zhong, 1998) support that idea that pollutants tend to be flushed from the basin on a daily basis. I have added the paper by Gaffney as support of this assertion. Still, I have taken pains to soften this assertion in the paper.

6) The single scattering albedo reported in Table 2 is significantly higher than what can be derived from the scattering and absorption coefficients reported by Baumgardner et al., 2000. Single scattering albedos can be derived that range from 0.7 to 0.85, but as

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shown in that paper, relative humidity plays a huge role, something not mentioned by the authors in the present paper.

61) We have taken the data from Dr. Baumgartner's paper, specifically the scattering and absorption coefficients from Figure 2, and shown that single scattering albedos derived under conditions of low relative humidity (as observed during our retrievals) match our single scattering albedo retrievals almost exactly, as noted in the revised manuscript. We have communicated with Dr. Baumgartner about his issue and he agrees with our conclusions.

62) This is a good point. When we recalculated the specific absorptions and the real part of the refractive index using the daily AERONET retrievals, the real part of the refractive index dropped to 1.39. (This is almost identical to the same quantity as inferred from the AERONET data, 1.40). Because the boundary layer is dry, it is unlikely that the aerosols are hydrated, and the best explanation for such a low refractive index is the presence of a large amount of OC, as noted in Salcido et al. (2005). This new finding has been brought out in the revised manuscript, Sec. 2.3.

63) It's true that the results are quite uncertain, and in the case of the lidar/aethalometer results, we can only report what we think is a lower bound. In regards to method II, only by assuming very dubious values of the density, refractive indices, etc. can one obtain values of the specific absorption outside the upper range of uncertainty (+40%). As noted in the conclusion, to obtain a specific absorption of 12.3 mˆ2/g for case number 6, one has to assume, for example, that the density of BC is 1.5 g/cmˆ3, and that the refractive index is 2.2 -1.2i (assuming no other sources of uncertainty). These values, or other combinations that provide a specific absorption of 12.3 mˆ2/g or greater, are outside the range thought plausible. Overall, the results suggest that the specific absorption is less than 10 mˆ2/g in the MCMA basin, consistent with the findings of Baumgartner et al. (2002).

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