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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.

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One of the main problems of determining black carbon (BC) mass specific absorption is the lack of a generally accepted standard for BC mass measurements. The manuscript is an interesting and useful contribution to the ongoing search for a more reliable method of measuring BC specific absorption. The text is well written and makes an essential contribution towards harmonizing two of the most frequently used methods for measuring aerosol optical properties. It should therefore be published with some corrections/modifications specified below.

Major Comments

1. Introductory remarks

The BC specific absorption coefficients of 7.5 and 9.2 mˆ2/g (at 500 nm) derived from methods I and II, respectively, are remarkably similar considering the fundamental difference in the two approaches. However, in light of the numerous assumptions and simplifications made in both methods one should consider these values 'effective' BC specific absorption coefficients. These values should be compared to previous studies in Mexico City and Metropolitan areas and a more thorough uncertainty assessment should be performed for both methods. I offer the following more detailed suggestions/comments for improving this manuscript:

2. Method I

Following referee #3 I request to estimate the overall uncertainty and consider the following aspects: 1) If possible, the vertical BC distribution within the well-mixed boundary layer (MBL) should be explored based on the lidar data and the lidar-induced measurement error should be estimated. 2) While the authors acknowledge some of the optical artefacts of an Aethalometer, a more rigorous discussion of the problems related to the conversion of light attenuation into BC concentration should be provided, in particular the uncertainties in BC specific attenuation coefficient due to optical artefacts and/or problems with the thermal desorption method used for EC mass determination (e.g. Weingartner et al., 2003, Petzold et al., 1997, Schmid et al., 2001). This will make it difficult to justify accuracies of BC mass to better than 20-30 %. 3) In order to reduce the shadowing effect the authors have chosen to reduce the maximum allowed Aethalometer attenuation from 25 to 10% (at what wavelength?). While this will reduce the average (over one filter cycle) shadowing effect (Weingartner et al., 2003), it is not an adequate measure to reduce the uncertainties in determining BC mass, since this and other systematic artefacts were supposedly. In fact reducing the maximum attenuation is expected to introduces slight positive bias in BC mass ($<$ 5 %; Weingart-

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ner et al., 2003). I do not recommend this practice, if the manufacturer-provided BC calibration factors are used.

The argument, that there is no absorbing aerosol layer above the MBL (P.4089, L.2-24) is absolutely crucial for inferring columnar BC mass according to method I. Therefore, I strongly recommend to strengthen this argument by a more explicit description of the underlying idea and by presenting all of the available evidence (without overstating the results). To clarify this request I offer the following outline for this paragraph: 1) In this simple two-layer model, the bottom layer (=MBL) is dominated by relatively fresh, local pollution with absorbing aerosols; the top layer (rest of optically relevant atmosphere) may (or may not) contain aged urban aerosols from the previous day(s) 2) Now one can imagine two extreme scenarios A) If the top layer is clean (i.e. the pollution from the previous day(s) was transported away) then the columnar omega_0 is well correlated with BC mass, since in general the background aerosol contains only weakly absorbing aerosol (omega_0 about equal to 1), i.e. any reduction in omega_0 can be attributed to MBL BC. B) On the other hand, if there is a highly absorbing residual top layer, the injection of absorbing aerosol into the MBL would not affect omega_0 very much, since both layers would roughly have the same omega_0 and therefore columnar omega_0 and MBL BC are expected to be NOT well correlated . Furthermore, the effect of a residual urban pollution layer above the MBL should be most pronounced on Good Friday, when there is almost no ground-level pollution. 3) Since MBL BC mass and omega_0 are well correlated (see Fig. 3), even on Good Friday, one can conclude that most of the columnar absorbing aerosol is represented by the MBL BC mass. However, one should acknowledge that this is not a very accurate way of proofing the absence of residual pollution layers above the MBL.

3. Method II

Again I concur with the request by referee #3 to explore the sensitivity of the results with respect to the rather substantial uncertainties in the index of refraction and density of BC. In addition, I suggest to also include the aerosol volume distribution into this

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effort.

The authors clearly identify the assumptions/simplification entering methods I and II. However, it seems to me that, for completeness, the list of assumptions entering the Mie calculations (p. 4091 L.12-16) should be expanded by three more items: 1) Uniform aerosol composition: this assumption was implicitly made by assuming that the BC volume fraction is independent of particle size (p.4093 L.15). Considering that BC is predominantly emitted in the submicron size range, this assumption is probably not well here, since the size distribution has about 50 % of its volume in the supermicron mode (p. 4092, L. 20-21). 2) Particle sphericity (core/shell Mie code): This assumption may be a rather severe approximation for relatively fresh soot emissions (as one might encounter in the vicinity of a city) due to the fractal nature of fossil fuel soot particles. 3) The empirical parameterisation of the average aerosol volume distribution reported by Dubovik et al. (2002) is representative for your case studies: It should be made very clear that the aerosol volume distribution was not explicitly measured, but inferred from a parameterisation based on the measured optical depth. For the applicability of the parameterisation, it is relevant that the optical depths encountered during the present study are well within the parameter range observed by Dubovik et al. (2002) and even close to the their arithmetic mean optical depth (0.43).

4. Results

As mentioned above based on the estimate of the measurement uncertainties in methods I and II the statistical significance of the observed differences in BC specific absorption should be assessed.

On several occasions the authors refer to method II as 'more rigorous' (e.g. p. 4084, L. 10) or 'less approximate' (e.g. p. 4090, L. 15) than method I mainly due to the uncertain vertical distribution of BC throughout the MBL. In light of the long list and in part rather severe assumptions/simplifications entering method II, I do not share this preference. Please substantiate this judgment more or remove it from the manuscript.

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Maybe in this context a brief summary of the main strengths and weaknesses of both methods would be helpful (maybe even in the conclusions section).

Please comment on how your results (mainly BC volume fraction and BC specific absorption) compare with other field studies in Metropolitan areas (especially Mexico City).

As mentioned above Figure 3 shows good correlation (give correlation coefficient) between columnar omega_0 and columnar BC mass. While I agree with the authors that this can be interpreted as evidence for the absence of optically absorbing aerosol layers above the MBL, I see no justification for the fit line, which suggests a linear relationship between omega_0 and BC mass as well as a background single scattering albedo of unity (omega_0 = 1 at BC mass = 0). The latter is certainly not true considering the ubiquitous nature of BC. Please either justify these implications or remove the fit curve from Fig. 3.

5. Conclusions The conclusions are concise and informative. I only suggest to revise according to the more detailed error analysis (as detailed above) and to include two important details regarding the data set: 1) effective sampling time (how many hours) and period (April 2003) and 2) the data set is limited to morning hours (7:30 - 12:00 local time) mainly prior to the deepening of the MBL, i.e. the derived parameters should not be mistaken for diurnal averages (although you could use method I to derive diurnal averages).

Minor Comments:

1. Title: 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 methods as measurement methods.

2. Abstract: I think the reader would understand better the main approach of the paper,

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if the keywords ‘Aethalometer’ and ‘Mie calculations’ were included to characterize methods I and II, respectively.

3. Please characterize the Aethalometer in terms of manufacturer, model and operating conditions (inlet cut-off diameter, sample flow rate, wavelengths, was the air dried?).

4. Briefly discuss the potential effect of inlet cutoff and line losses on the Aethalometer signal considering that about half of the columnar aerosol volume is in the coarse mode with a modal (volume diameter) at about 5 micron (see parameters in Eq. 3)

5. p. 4088 L. 6-7: ‘Mixing commences prior to noontime’: In addition to Fig. 1 I suggest you also refer to Fig. 2, which provides more direct evidence for this statement.

6. The authors interpret the 10-20 % positive bias of the height of the MBL determined by the lidar compared to the one derived from the potential temperature profile as statistically significant (p.4088 L. 26-29). This statement should be substantiated by an assessment of the estimated experimental uncertainties.

7. P. 4087, L.13-20: To understand this argument regarding the refractive index of BC one also has to mention that A) the internal data processing algorithm of the Aethalometer scales the specific attenuation coefficient determined at 880 nm to arbitrary wavelengths assuming a 1/lambda dependence of the and B) Mie calculations for particles with constant index of refraction show that in the small particle limit (usually met for fossil fuel soot particles) spectral absorption is proportional to 1/lambda .

8. P. 4088, L 24: The MBL ‘collapses quickly’. This is a misleading statement, since the layer does not actually collapse (which would lead to an increase of all extensive parameters in the MBL), but rather a new, relatively shallow, nocturnal boundary layer is formed after sunset from the ground up due to surface cooling (escape of long-wave radiation) and subsequent cooling of the low level air.

9. In Eq. 3 you introduce sigma as ‘standard deviation’, while it actually represents ln(sigma_g), where sigma_g is the geometric standard deviation. I realize that Dubovik

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et al. (2002) made this rather unconventional choice, but I suggest you clarify this issue with a footnote.

10. P. 4096, L. 3-17: This section should be shortened considerably. The 1/lambda dependence of specific absorption by urban aerosols is well accepted and you only have to refer to your finding from P. 4087, L. 17-20, to confirm this dependence directly from your Aethalometer data.

11. P. 4099: Here you raise the issue of a potential impact of OC on the photometer data, but never discuss it. This can be easily done by again referring to your finding from P. 4087, L. 17-20 (specific absorption varies with 1/lambda) which rules out a significant OC contribution to aerosol absorption, since OC displays a significantly steeper lambda-dependence (Kirchstetter et al., 2004).

12. P. 4100: Having provided such a detailed comparison of method II and the Schuster et al. (2005) AERONET results, it would be appropriate to close this section with a summarizing remark.

13. P. 4100, L.24. Here it sounds to me, as if you used concomitant AERONET data to retrieve aerosol volume distributions, which -according to p.4092 - you did not. Please make sure that the (quick) reader (who only reads abstract and conclusions) understands that you used a parameterisation by Dubovik et al. (2002) to infer the columnar aerosol volume.

14. Table 1 should also include some details about the Aethalometer (model, wavelengths, etc.)

Typos:

1. P. 4084 L. 4: replace ‘BC carbon’ by ‘BC’

2. P. 4090 L. 14: ‘most’ should read ‘more’

3. P.4090 L. 14: insert ‘and’ prior to rV

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4. P. 4092 L. 15: ‘the is’ should read ‘is the’

5. P. 4093 L. 16: insert space before ‘are’

6. P. 4094 L. 14: replace ‘for’ by ‘from’

7. P. 4095 L. 3: replace ‘show’ by ‘shows’

8. P. 4095 L. 7: replace ‘show’ by ‘shows’

9. P. 4095 L. 16: At ‘ages1’ what does the superscript refer to?

10. P. 4096 L. 16: Remove ‘s’ from ‘conversions’

11. P.4096 L. 24: Please also mention the moment of the size distribution this radius is referring to (I assume: number size distribution). The word ‘conventional’ is not needed.

12. P. 4097 L. 26: Replace ‘converted values appropriate for’ by ‘converted to’

13. P. 4098 L. 9: Remove one of the two ‘are’

14. P. 4101 L. 9: It would help the (quick) reader, if you would identify the wavelength here (500 nm).

References (if not provided by Barnard et al.)

Kirchstetter, T. W., Novakov, T., and Hobbs, P. V.: Evidence that the spectral dependence of light absorption by aerosols is affected by organic carbon, J. Geophys. Res.-Atmos., 109, doi:10.1029/2004JD004999, 2004.

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