

Interactive comment on “Assessment of the sensitivity of core/shell parameters derived using the single-particle soot photometer to density and refractive index” by J. W. Taylor et al.

Anonymous Referee #2

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General comments

This paper promises to assess the sensitivity of SP2-derived black carbon (BC) aerosol coatings to assumed density and refractive index. The analysis presented is decent and good arguments are made for using certain values of density and refractive index over other values; however, the results are not really presented as a “sensitivity.” Overall, the paper falls far short of a complete sensitivity analysis as is promised by the title and abstract. I hope the authors do a detailed sensitivity analysis and majorly revise the manuscript to fit the title, rather than scale back the scope of this study. I believe there ought to be sufficient data in this dataset to perform such an analysis.

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A more complete sensitivity analysis should include a more systematic variation of the input parameters rather than choosing just six values from the literature. The refractive index should be separated into real and imaginary parts and the sensitivity to each part should be assessed. In addition, sensitivity to the coating refractive index should be assessed. The constraint on coating refractive index from co-located measurements of composition by the SP-AMS can be used to assess accuracy, but it is still of interest to assess the sensitivity to this parameter as well.

Speaking of accuracy, throughout the current manuscript, it is reported that an accurate determination of mixing state can be made with proper input parameters. However, accuracy is never proven. To prove parameter accuracy, another independent measurement is needed, such as the co-located bulk optical property measurements. A forthcoming JGR paper by the same authors (Taylor et al., 2014) may address some of my concerns about accuracy, but this was impossible to assess in this review. If a discussion of accuracy is to be kept in this study, some of the optical property data seems necessary to include in *this* manuscript.

Similarly, a detailed discussion of the sensitivities within the SP2 itself should be added. This discussion is partially addressed with the section on notch location, but this could be much more complete. For example, taking the minimum detectable change in scattering intensity (2.44 mV from the APD), what is the minimum detectable difference in scattering cross section? All else being equal, how does this translate to core size or coating thickness?

The paper is decently written for the most-part, but there are quite a few technical corrections listed below that are meant to make the wording more precise and clear. For example, use of the word “this” as the noun in a sentence should be avoided. While I find no major errors in the analysis presented, I do find it a bit lacking for a complete “sensitivity analysis” and, thus, I recommend a major revision before publication.

Taylor, J. W., J. D. Allan, D. Liu, M. Flynn, P. L. Hayes, J. L. Jimenez, B. L. Lefer, N.
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Grossberg, J. Flynn, J. Gilman, J. A. de Gouw, and H. Coe (2014) Comparison of measured black carbon mass absorption coefficient to modelled values during CalNex 2010, *J. Geophys. Res. Atmos.*, in preparation.

Specific comments

Title : To me, the wording is a bit confusing. In my opinion, it would be better to move “to density and refractive index” to immediately after “sensitivity.” Also, because sensitivity is not rigorously explored in this paper, consider a new title if the scope of this paper remains largely unchanged throughout this review process.

pg 5492 - line 16 : In many places throughout the manuscript (I won't list them all), you use the wording “coating thickness distribution” and then quote a single number with a standard deviation. Is this really a “distribution?” It seems like it would be more accurate to say that this number is a mean value plus-minus one standard deviation. If, instead, you mean that this value is the peak location of a Gaussian and the plus-minus value is the width of the Gaussian then it must be made clear in the text what you are reporting.

5492 - 17 : How do you know the determination of mixing state is accurate? Do you have an independent measure of mixing state that you can directly compare to your results? In the manuscript, it seems like you assess accuracy as a situation that makes sense or sounds reasonable (that is, fresh BC that passes through a thermodenuder ought to have little if any coating) and whatever parameters gives this most-likely situation is “accurate.” To truly assess accuracy, you need to have an independent measurement that you can quantitatively compare to the derived mixing state in this paper. This independent measurement could be those co-located optical property measurements, which I assume are all presented in Taylor et al., 2014. To keep these “accuracy” statements in this manuscript, you will need to bring in some of the data from your other

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pending paper.

Taylor, J. W., J. D. Allan, D. Liu, M. Flynn, P. L. Hayes, J. L. Jimenez, B. L. Lefer, N. Grossberg, J. Flynn, J. Gilman, J. A. de Gouw, and H. Coe (2014) Comparison of measured black carbon mass absorption coefficient to modelled values during CalNex 2010, *J. Geophys. Res. Atmos.*, in preparation.

5492 - 19-20 : The fact that the precision remains the same regardless of what parameters are used in the core/shell model simply means that whatever variation or noise exists in the retrieved coating thicknesses is a result of noise in the raw measurement. This point should be made clear in the paper. Also, it would be nice to assess the sensitivity of the retrieved coating thickness to incandescence versus scattering noise.

5497 - 5 : Put your calibration with glassy carbon spheres in context of the fullerene/aquadag discussions found in Baumgardner et al., 2012 and Laborde et al., 2012. I see you mention it briefly in the supplemental section, but I think its important enough to mention in the main manuscript and maybe expand the discussion in the supplemental to include an estimate of the bias you would expect by calibrating with glassy carbon spheres versus the other materials.

Baumgardner, D., O. Popovicheva, J. Allan, V. Bernardoni, J. Cao, F. Cavalli, J. Cozic, E. Diapouli, K. Eleftheriadis, P. J. Genberg, C. Gonzalez, M. Gysel, A. John, T. W. Kirchstetter, T. A. J. Kuhlbusch, M. Laborde, D. Lack, T. Müller, R. Niessner, A. Petzold, A. Piazzalunga, J. P. Putaud, J. Schwarz, P. Sheridan, R. Subramanian, E. Swietlicki, G. Valli, R. Vecchi, and M. Viana (2012) Soot reference materials for instrument calibration and intercomparisons: a workshop summary with recommendations, *Atmos. Meas. Tech.*, 5, 1869–1887, doi:10.5194/amt-5-1869-2012.

Laborde, M., P. Mertes, P. Zieger, J. Dommen, U. Baltensperger, and M. Gysel (2012)

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5497 - 8 : This wording makes it sound like your SP2 was plus-minus 10% of NOAA's SP2. However, in the supplemental section, you more clearly state that there was a systematic offset, which is what I would expect given your calibration material. Also, in the supplemental section, you further develop the uncertainty estimate to 14%, but never mention this in the main manuscript. You need to more clearly state your total uncertainties and biases in the main manuscript to bring the discussion in line with your supplemental section.

5497 - 14-15 : Quote the average correction factor (4.6% from the supplemental section) here. Also clarify by stating in the manuscript that the correction was done by fitting the measured mass distribution to the sum of two Gaussian distributions. In fact, exactly how this correction was done was not very clear in the supplemental section A2 and should be improved as well.

5497 - 28 to 5498 - 1-3 : The rBC convention is also used for the SP2, as you state on page 5494 - line 18. Why do you say the SP-AMS and SP2 aren't measuring the same material? By using the same laser, they should be measuring the same material. If you mean that the laser powers may not be equal and therefore the incandescence temperatures reached in each instrument is different, then you need to clearly explain this. If you mean that the sum of the carbon clusters in the mass spectra are not equivalent to the incandescence signal in the SP2, then you need to clearly explain this.

5498 - 24-25 : Why do smaller particles have higher rBC to coating mass ratios?

5498 - 29 : Why didn't you study the sensitivity to shell refractive index, especially since you recognize a known bias? I think that this should be examined in order to fully understand all the sensitivities involved in the core/shell retrieval technique with

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the SP2.

5499 - 2 : Can you argue that accumulation mode particles are more important for light scattering than smaller particles and so your derived shell refractive index may turn out to explain bulk optical properties pretty well anyways?

5503 - 25 : To be clear, are you talking about the notch when the signal changes direction or do you mean when the signal crosses zero? Gao et al., 2007 shows a notch in the signal that is different than the smooth crossing of zero.

Gao, R. S., J. P. Schwarz, K. K. Kelly, D. W. Fahey, L. A. Watts, T. L. Thompson, J. R. Spackman, J. G. Slowik, E. S. Cross, J.-H. Han, P. Davidovits, T. B. Onasch, and D. R. Worsnop (2007) A novel method for estimating light-scattering properties of soot aerosols using a modified single-particle soot photometer, *Aerosol Sci. Technol.*, 41(2), 125–135, doi:10.1080/02786820601118398.

5504 - 11 : Looking at the time-dependent scattering cross section is a different technique than the leading-edge only method described in the rest of this section. If you used this other technique, you need to describe it in a lot more detail, at least in the supplemental section if not in main manuscript.

5504 - 18 : Is "baseline" really the zero signal line? If this is true, then instead of using the zero-crossing position are you using 20 units above zero (positive signal)? I don't think this is the case because it doesn't make sense based on the ambiguity that you describe that you are trying to resolve. Clarify this paragraph.

5506 - 18 : Are there any references that support this claim? From Figure A1, 135 - 200 nm does not cover the "majority" of the size distribution of the cores.

5507 - 12 : Do you know for sure the APD's collection angles and alignment well enough for a 1 nm accuracy on your measurement? I would be surprised if this was true - if it is, you need to prove it in the manuscript or provide a reference to someone who

C1538

has proven this accuracy. When assessing the sensitivity of your retrieved core/shell parameters, it is important to recognize the physical limitations of the instrument itself and not overstate its theoretical accuracy.

5507 - 24-26 : What happens if you adjust the density and refractive index of the core such that the negative coatings are eliminated and the Mie lookup tables give a coating thickness of zero? What would the density and refractive index need to be? Please add a discussion of these numbers and their plausibility for ambient BC.

5509 - 4 : Doesn't Figure 4b show that the fraction of particles with $E_{sca} < 1$ is actually *not* strongly dependent on density?

5509 - 6-7 : What is the "similar technique" you are referring to? Did you actually *measure* density and refractive index? If so, what method did you use?

5509 - 16-18 : There should be more analysis here. If you truly intend to present the "sensitivity" to density and refractive index, then you need to quote a sensitivity, which is $\Delta E_{sca} / \Delta(\text{density})$ and $\Delta E_{sca} / \Delta(\text{refractive index})$. From Figure 4b, the sensitivity to density is small, and from Figure 4c, the sensitivity to refractive index will be larger - but we need numbers here. This is also a good place to quantify the width of the distribution in order to prove that density and refractive index are *not* changing the shape of the distribution, just the offset.

In Section 3.6, you derived a density and refractive index for fresh BC by finding literature values that made the Mie model "behave" like you think it should. This analysis does not prove that these are the absolute best values to use for fresh BC in this study - these values are merely the "most appropriate" (5509 - 10) of the values you tested. Also, it is incorrect to say that "all other parameters lead to an overestimation of E_{sca} " (5509 - 13-14) because you did not test *all* other parameters, just several that you found in the literature.

Several outstanding questions remain: How applicable are these parameters to aged

C1539

BC that has been structurally rearranged? Does the thermodenuder do anything to fresh, uncoated BC that might change these results versus sampling fresh BC without the thermodenuder?

5510 - 1 : How do you get from mass density to refractive index? More details are needed in this section.

5510 - 7-8 : How big were the changes in refractive index? Were these changes significant? The standard deviation seems small, but there's no information provided that helps us assess whether a 0.01 change is significant or not. Most importantly, there is no work done to show the sensitivity to the coating refractive index of the derived coating thicknesses in Section 3.9. Constraining your coating fits with co-located measurements is the right thing to do, but you should also present the sensitivity to the coating refractive index and an estimate of the error on this number based on any assumed errors in the SP-AMS measurements.

5510 - 24 : How do you assess "accuracy?" Use of this word implies that you know the morphology and size of BC for certain. Supplementary Section A1 does not list "~3%" anywhere - it is listed as "~2.5%." Also, ~30% is not the statistical uncertainty but the absolute uncertainty. Statistical uncertainty is the variation over a time period, which the supplementary section quotes as ~2.5%. Absolute uncertainty is the uncertainty away from the true BC mass for any given measurement and exists because we don't know the morphology, density, and refractive index of the calibration material relative to ambient BC.

What about uncertainties from the chosen calibration materials? You should discuss the uncertainties resulting from use of glassy carbon spheres.

5511 - 12 : Did you work out the overall uncertainty? If you did it is not clear. In supplemental Section A1, it looks like you convolve the 10% systematic difference between your SP2 and NOAA's SP2 with a 10% uncertainty based on your chosen calibration material, but you never use the 30% per-particle mass uncertainty.

C1540

5511 - 24 : How do Gaussian fits to the data yield accuracy and precision?

5512 - 4-5 : Again, how do we know this technique is accurate?

5512 - 8-9 : See note above for page 5492 - lines 19-20.

5512 - 10 : The way Figure 6 is presented may be systematic in refractive index but not in density. Again, you haven't really explored sensitivity in a systematic way - these would need to be presented much like Figures 4b and 4c, where you hold one parameter constant and vary the other. You should also vary the values systematically and not just use six selected values.

How does Figure 6 look if you separate fresh and aged air masses rather than use the whole campaign?

5513 - 13 : The mention of CCN activity seems out-of-the-blue here. What connection does any of the rest of the manuscript have to CCN activity?

5513 - 16 : Actually, you have not demonstrated anything about optical properties and have only pointed to another "in preparation" paper you are working on. To make this claim, you need to take your derived coating thicknesses and calculate optical properties and show the differences resulting from the different coating thicknesses retrieved.

5513 - 17 : Also, your data do *not* show a strong sensitivity to rBC core density.

5513 - 24 : Again, you have not proven that the SP2, even with the proper input parameters, can accurately determine mixing state.

5514 - 6-8 : This sentence presents a new idea. You should explain how a new SP2 will improve precision.

C1541

Technical corrections

pg 5492 - line 17 : "This" means what exactly? Be more specific and precise in your wording. Below, I will list many more places in the manuscript where you used "this" as a noun, but I may not have caught them all. Please carefully proofread your final manuscript to remove all use of "this" as a noun.

5493 - 12 : Is the "concentric core/shell model" the Mie model? Need a reference here.

5493 - 20 : "Californian" should be "California"

5493 - 22 : "or" should be "and"

5493 - 25 : Need to add the year to the Cappa et al. reference.

5495 - 11 : Should reference the CalNex overview paper, Ryerson et al., 2013.

Ryerson, T. B., A. E. Andrews, W. M. Angevine, T. S. Bates, C. A. Brock, B. Cairns, R. C. Cohen, O. R. Cooper, J. A. de Gouw, F. C. Fehsenfeld, R. A. Ferrare, M. L. Fischer, R. C. Flagan, A. H. Goldstein, J. W. Hair, R. M. Hardesty, C. A. Hostetler, J. L. Jimenez, A. O. Langford, E. McCauley, S. A. McKeen, L. T. Molina, A. Nenes, S. J. Oltmans, D. D. Parrish, J. R. Pederson, R. B. Pierce, K. A. Prather, P. K. Quinn, J. H. Seinfeld, C. J. Senff, A. Sorooshian, J. Stutz, J. D. Surratt, M. Trainer, R. Volkamer, E. J. Williams, and S. C. Wofsy (2013) The 2010 California Research at the Nexus of Air Quality and Climate Change (CalNex) field study, *J. Geophys. Res. Atmos.*, doi:10.1002/jgrd.50331.

5495 - 14 : Replace "campus, Pasadena" with "campus in Pasadena"

5495 - 16-17 : Is this chemical, photochemical, or physical processing?

5495 - 26 : "This" means what exactly?

5496 - 2 : Remove "these"

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5496 - 4 : Strictly speaking, the PASS-3 is not a “BC instrument.” Need to make the wording here more accurate.

5496 - 5 : Add the aethalometer manufacturer and model number.

5496 - 9 : What is meant by “NOAA” in this sentence? Did NOAA setup and operate the inlet you tapped into, or is this a specific inlet built and used many times on NOAA field campaigns? Please clarify and add a reference if it is a specific inlet that has been used previously.

5496 - 17 and 19 : “PASS” should be “PASS-3.” There may be other locations in the manuscript where this mistake is made.

5496 - 23 : “light” should be “laser”

5497 - 12-14 : Be more accurate in your wording - the detectors measure single particles with a mass between those numbers you quote.

5497 - 25 : Be more accurate in your wording - the laser vaporizes refractory species (most of which is BC).

5498 - 6 : I think “a rBC” should be “an rBC”

5498 - 16 : Clarify that “other components” are in the aerosol.

5498 - 21-22 : Clarify this sentence - the relative concentrations are BC to organics and inorganics within the particle and are not relative in time.

5499 - 11 : “PASS” should be “PASS-3”

5500 - 17 : “from” should be “for”

5500 - 21 : “Whilst” should be “While”

5501 - 8 : “there is question” should be “there is a question”

5502 - 13 : What is “this” technique? Rayleigh scattering or Mie scattering? Clarify this

C1543

section.

5503 - 22 : “twin-” should be “two-”

5504 - 9 : By “laser intensity” do you mean “scattered intensity”? You are considering data up to 5% of the peak scattered signal for that particle, correct?

5504 - 10 : “This” means what exactly?

5505 - 19-21 : Note that the thermodenuder settings have nothing to do with the age of the particles - need to reword this sentence and other places in the manuscript and figure captions to clarify this point.

5506 - 17 : “Whilst” should be “While”

5507 - 2 : The scattering model is the Mie model, not the Gao model. This reference needs to be changed.

5507 - 12 : Reword the sentence so that it does not begin with “600 nm.”

5507 - 17 : Isn't the “most basic product” of Mie theory the scattering cross-section? Consider rewording this sentence.

5508 - 24 : What is a “significant change” in coating thickness? Please give numbers.

5509 - 6 : The word “encouraging” is a matter of opinion - reword this sentence to be objective.

5509 - 11 : Remove the comma after “dataset” and remove the word “likely”

5509 - 15 : Remove the comma after “enhancement”

5510 - 4 : “this approach” is what exactly?

5510 - 18 : By “laser power” do you mean “scattered intensity”?

5511 - 14 : What does “spread” mean? Is it error, uncertainty, or width of a Gaussian fit to the data?

C1544

5512 - 4 : "This" means what exactly?

5512 - 13-16 : This sentence is confusing and needs to be reworded.

5512 - 16 : "This" means what exactly?

5513 - 1-3 : This sentence is confusing and needs to be reworded.

5513 - 13 : "This" means what exactly?

5514 - 12 : "increase" should be "increased"

5514 - 14 : "refractive" should be "refractive index"

5514 - 15 : Remove the comma after "datasets"

5514 - 18-21 : This sentence is confusing and needs to be reworded.

5525 - Figure 1 : Consider using color and different types of dashed lines instead of different weights of solid black lines. The difference in 1/4 inch and 3/8 inch is especially hard to see. Also, what is "- outer diameter?"

5526 - Figure 2 : Consider using a thick dashed while line to represent the saturation of the scattering detector; the black line can be hard to see amidst all the color.

Supplemental section comments

page 2 : How was the stability of the incandescence channel assessed during the experiment?

page 2 : Is the 30% per-particle mass uncertainty used in the assessment of errors in the rest of the paragraph?

page 2 : Is the 10% uncertainty due to calibration material a systematic error as well?

C1545

How do you know the diesel soot type you need to match to Is the same as in Laborde et al., 2012?

Laborde, M., P. Mertes, P. Zieger, J. Dommen, U. Baltensperger, and M. Gysel (2012) Sensitivity of the Single Particle Soot Photometer to different black carbon types, *Atmos. Meas. Tech.*, 5, 1031–1043, doi:10.5194/amt-5-1031-2012.

page 2 : Does the systematic uncertainty of 14% mean that your SP2 is measuring 14% more per-particle mass than you believe is actually there in the ambient BC? Do you correct for this bias when determining the proper input parameters in the main manuscript? What effect would this bias have on your retrieved coating thickness?

page 4 : Is "average" actually "campaign average?"

page 4 : What is "high-HDDV" mean?

page 4 : Was rBC mass concentration ever reported in the main manuscript?

page 9 : By "enhance" do you mean that you expect to have more or fewer problems with the particle focusing in your AMS chamber?

page 12 : The fractional composition at higher thermodenuder temperatures is a bit concerning. It sounds like what is happening is that at higher temperatures, the rBC is changing somehow such that its not showing up in the mass spectra where it should be. If the rBC is, in fact, changing chemically, doesn't it make sense that it might be changing optically as well? If so, this could affect your "most accurate" results for fresh BC, especially because you derived this result at the highest temperature settings on the thermodenuder.

Interactive comment on Atmos. Meas. Tech. Discuss., 7, 5491, 2014.

C1546