Atmos. Chem. Phys. Discuss., 12, C12727–C12734, 2013
www.atmos-chem-phys-discuss.net/12/C12727/2013/

Atmospheric
Chemistry
and Physics
Discussions

Interactive comment on "Effects of internal mixing and aggregate morphology on optical properties of black carbon using a discrete dipole approximation model" *by* B. Scarnato et al.

B. Scarnato et al.

barbara.v.scarnato@nasa.gov

Received and published: 18 February 2013

Reply to Comments from Referee #3

The authors greatly appreciate the constructive comments from the reviewer. The reviewer notes that our results are very useful to the study of aerosol climate effects and improving the accuracy of aerosol remote sensing retrieval. The referee recommended publication of our manuscript after revision that addresses the following comments. Our response to each comment is discussed below. We revised our manuscript in a number of locations in response to the reviewer's comments. The specifics are listed below.

- Comment #1 What is the difference between NaCl-containing mixture and sulfate-containing mixture? Previous studies (e.g., Kahnert et al, 2012, see reference on p. 26420) have discussed the aerosol optical properties (AOP) of BC aggregate encapsulated in sulfate shell using DDA method. The morphologies and refractive indices of such simulated aerosol models are quite close. With the same DDA algorithm, the optical properties of NaCl-containing mixture and sulfate-containing mixture should be similar. Though the optical characteristics of BC internal mixed with NaCl may be useful for coastal areas, the support experimental data is lack.

Response: We agree with the referee that optical properties of BC aggregates internally mixed with NaCl and sulfate should be similar, as refractive indexes are similar and smoothed edged characteristics of NaCl morphology (but not of sulfate morphology) do not introduce strong features in the optical properties.

It is not straightforward to compare our results with those of Kahnert et al, (2012) because the size and shape of the BC cores and mixing ratios are different. Kahnert et al state “the absorption is more sensitive to the relative size of the core and the shell than to the position of the core within the shell.” Kahnert et al present at select wavelengths cross sections for a composite of size distributions, varying the size of the BC aggregates and the size of the total particle, while keeping constant the mixing ratios between BC an sulfate. We do not have matching cases with same size and shape of BC core and size of the total particle.

Nonetheless, we roughly compared the most similar case presented in Table 1 of Kahnert et al (Number of BC monomers N=102 and R =200nm) with our internally mixed case FIS (N=82 and R= 138nm). The SSA values presented in our study have the same order magnitude as those presented by Kahnert et al.

Regarding a lack of evidence of mixed NaCl/BC particles, we note that a number of studies provide supporting evidence of internally mixed NaCl and BC particles to justify our study, as follows.

Samples collected during the Carbonaceous Aerosols and Radiative Effects Study

(CARES), carried out in June 2010 in Central Valley, California, demonstrated that marine aerosol interacts with anthropogenic pollutants (Laskin et al., 2012). Particles sampled during CARES were internal mixtures of aged sea salt, sulfates, and carbonaceous particles. Laskin et al. 2012 also compared the composition of particles collected in a pristine marine location (Point Reis National Seashore in California) and during the CARES campaign. During CARES, NaCl-containing particles had a more significant carbon fraction than the marine particles in the pristine location.

Li et al, 2003 show SEM images of mixed NaCl/soot particles collected in Sagres in Portugal, as a part of the Aerosol Characterization Experiment (ACE-2 in 1997). The mixing state is representative of our case study b) in Figure 4 identifying BC immersion and surface contact with NaCl

Smirnov et al, (2011) and Pace et al., (2006) also found evidence of mixing of sea salt marine aerosol with anthropogenic aerosol in interpreting radiance measurements from the Maritime Aerosol Network.

Further, several modeling studies (i.e. Chandra et al., 2004, Aquila et al., 2011, Flanner et al., 2012) looked at the effect of BC mixing with NaCl on both radiative fluxes and Atmospheric Chemistry global models.

To clarify this point, we have modified our manuscript as follows:

On page 2 of the revised paper, the following sentence was added. “When aerosols are transported far from their emission sources, their climatic and environmental impacts are delocalized from their source regions (Kanakidou et al., 2005; Pace et al., 2006; Smirnov et al., 2011)”

On page 4 of the revised manuscript: We added the following sentence. “Chemical aging and atmospheric processing of sea salt particles may take place in many geographic areas where marine aerosol interacts with anthropogenic pollutants (Laskin et al., 2012, Li et al., 2003, Pace et al., 2006 and Smirnov et al, 2011)”

On Page 9 in the section “BC internally mixed with NaCl” of the revised manuscript we added the following sentence: “SEM images of aerosol samples from field campaigns, including the second Aerosol Characterization Experiment (Li et al., 2003) and the Carbonaceous Aerosol and Radiative Effects Study (Laskin et al., 2012), show sea salt aerosol (NaCl) with a smoothed cubic/rectangular prism shape, internal mixtures of NaCl with BC aggregates, and NaCl/BC mixtures with features similar to those observed in our samples, with a partial inclusion and partial surface contact of BC on the NaCl surface (Figure 4b).”

On page 34 of the revised manuscript, we added the following references: Kanakidou et al., 2005, Laskin et al., 2012 and Li et al., 2003.

- Comment #2 In Tab.1 and 2 (P.26424-26425), the comparisons of bare BC and mixtures are not distinct. The input parameters of those bare BC aggregates (e.g., Nm, P) are similar. The monomer numbers of those BC aggregates are also small. If the Nm=50, 100, 200 and 500, the results of those aggregates can be more persuasive. Moreover, the optical properties are averaged for 64 random target orientations in this paper. Kahnertet al computed the sulfate-containing mixtures with 864 discrete angles for obtaining accurate orientation-averaged results. The fewer monomer numbers may lead to less random orientations needed. Furthermore, the porosity of the BC aggregates is introduced for the measurement of the compactness. The commonly used Df should be listed in Tab.1 and 2 if possible to validate it.

Response: The number of monomers discussed in the paper are consistent with the particles that we generated in the laboratory from a combustion flame, as observed by electron microscopy. More importantly, we find agreement between our modeled MAC and SSA values and those measured in other studies.

Our modeled SSA values agree with the values reported in literature (0.25 +/- 0.05 at 550 nm). In all the cases presented in this paper, MAC lies between 6.3 and 7.0 m2/g at 550 nm, in agreement with the range of values reported by Bohren and Huffman (1983); Martins et al. (1998); Fuller et al. (1999); Bergstrom (1973); Bond and Bergstrom (2006); Adachi et al. (2007). For aggregates with a much larger number of monomers (600) than those modeled in this study, Kahnert (2010b) estimated MAC values (at 550 nm) of 5.2 +/- 0.1 m2g$-$1 for lacy aggregates, 4.9 +/-0.1 m2g-1 for compact aggregates, and 3.3+/- 0.4 m2g-1 for spheres.

We do realize that the typical number of monomers in a BC aggregate is matter of current debate. At the AGU Fall meeting 2012, we discussed this issue with Dr. Buseck and Dr. S.K Mishra. At the same meeting, Dr. Mazzoleni and others presented images of black carbon aggregates from the Las Conchas wildfire on June 26, 2011 in New Mexico. BC aggregates showed an average of 103 monomers, which agrees with our estimates of the number of BC monomers in aggregates produced by flame.

The fractal dimension “Df” is a variable that has been commonly used when describing fractal aggregates. Df is described in Equation 1 in the manuscript. When Df is calculated for a single particle (not a population), Df is dependent on a pre-defined value of the structural coefficient “k0” which is typically assumed to equal about 1.2. However, there is no universal agreement regarding the value of K0, and uncertainty in k0 may affect the Df value. The following papers enforce this position.

1. Brasil et al., 1999 (cited in our the manuscript) discuss the variability of k0 for BC aggregates. 2. Tomography measurements suggest higher values of the fractal dimension and lower values of structural coefficient (Adachi et al., 2007). 3. Chakrabarty. et al., 2011 state that “There is no universal agreement regarding the value of k0, and a wide range of k0 values (between 1.1 and 8) has been reported so far (Farias et al. 1995; Sorensen and Roberts 1997; Heinson et al. 2010). 4. In a recent simulation study, Heinson et al. (2010) showed that aggregates of a broad range of shapes all with Df ≈1.8 independent of their shape, but with a shape-dependent k0.”

Therefore, we do not consider the fractal dimension a reliable method to describe fractal aggregates and we prefer to describe aggregates in terms of porosity. The above

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

citations are added in the revised paper on page 5 at line 134.

The comment regarding the number of random target orientations (originally 64 in our paper) was also raised by another reviewer. In response, we re-computed all optical properties including scattering phase function and degree of linear polarization for 1000 and 3000 target orientations. We found that 1000 and 3000 orientations converged on the same solutions. There were small differences between solutions obtained with 64 and 1000 target orientations, but none of our conclusions have changed. We revised the paper and now report optical properties for 1000 orientations, and we include the results of this sensitivity analysis, as follows.

We modified line 188-193 in the revised paper with the following sentence: “Reported optical properties are the average values computed for 1000 random target orientations (Kahnert et al., 2012) and 9 multiple scattering planes that satisfy the condition $|m|kd < 0.3$. Optical properties were also computed for 64 (according to Shen et al. (2008, 2009)) and 3000 orientations.

As noted below, we found that 64 target orientations were sufficient to converge on the optical properties (i.e., MAC and SSA) of bare and internally mixed compact aggregates, but a larger number of orientations was required to attain converged orientation averaged values of the MAC of internally mixed lacy aggregates. Predicted optical properties using 1000 target orientations are consistent with results using 3000 orientations.”

Results for 64 and 100 orientations are discussed in the revised paper at line 260. “Absorption amplification factors computed as MAC(λ)mixture/MAC(λ)bare at a λ = 550 nm are listed in Table 2. We also computed absorption amplification factors averaged over the 200-1000 nm range, which were 1.0 ± 0.0 for lacy BC aggregates partially included in NaCl (case FIS), 1.7 ± 0.1 for lacy BC aggregates fully included in NaCl (case FI), 1.4 ± 0.1 for compact BC with an inclusion of NaCl (case GIS), and 2.2 ± 0.2 for compact BC aggregates fully immersed in NaCl (case GI). The amplification factors stated above correspond to optical properties averaged over 1000 target orientations. Amplification factors computed using 3000 target orientations were the same. Amplification factors computed using 64 target orientations were the same as those stated above for compact BC aggregates (cases GIS and GI), but were slightly higher for lacy BC aggregates: 1.1 ± 0.0 for case FIS and 2.0 ± 0.1 for case FI. This illustrated the significance of using a sufficient number of target orientations to converge on predicted optical properties using DDSCAT."

We find that the spectral features of S11 and -S12/S11 are maintained at 466 and 733 nm, using either 64 or 1000 orientations, but the magnitude may vary in the backscattering range between 100 and 180 degrees.

- Comment #3 Fig.1 (P.26426) can hardly show the lacy and compact structures from SEM images. Both bare BC aggregates are chain-like clusters. In my opinion, the main difference between the two images is the monomer numbers. However, the Fig.2 (P.26427) can effectively depict the compactness of bare BC models. Thus, the image of compact BC aggregates should be replaced as the right SEM image in Fig.1.

Response: We agree with the reviewer that the main features in Figures 1a and 1b are chain-like clusters. These figures also show BC clusters that are compact. To clarify, we have re-stated the caption to Figure 1 as follows:

"Fig 1. Two SEM images of bare BC aggregates. In each image, two types of morphologies are evident: chain-like (lacy) structures and compact structures."

- Comment #4 In Fig.3 (P.26428), these curves computed discretely, what is the spectral resolution? If the spectral samples are few, please mark those points in figures, or explain these wavelengths in detail. Meanwhile, the curves in Fig.3a are close, so different line styles are needed, or the morphologies of models can be simulated more different.

Response: The spectral resolution is 100 nm. We added this information to the caption of Figure 3. In Figure 3a, the lines are close for wavelengths larger than 500 nm b/c MAC values are very similar. There distinction is much clearer where it matters, for wavelengths smaller than 500 nm.

- Comment #5 The internal mixing types of BC aggregates and NaCl are three, as shown in Fig.4. Why ignore the type (c) in simulation and analysis? NaCl immersion in BC would be different from the bare BC aggregates and other mixtures. It can be useful for the BC aggregates with considerable monomer numbers with smaller NaCl particles.

Response: Type c was simulated. This is discussed in the manuscript and is shown in Figure 6 case b.

- Comment #6 In Fig.8 and 9 (P.26433-26434), the X-axis should be set from 0 to 180 degree. Please mark 180 degree for these figures. And the legend is not proper located for Fig.8b.

Response: Agreed and fixed.

Interactive comment on Atmos. Chem. Phys. Discuss., 12, 26401, 2012.