Reply to Comments from Referee #1

The authors greatly appreciate the constructive comments from the reviewer. The reviewer notes that our study has interesting results which reveal the importance of BC morphology and mixing states for its light absorption and has implications in climate modeling and remote sensing measurements. The reviewer asked us to address a number of comments to enhance the importance of the manuscript prior to publication. 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

Why NaCl particles are chosen? Although the reasons are explained in p 26407 and 26413-26414, yet mixtures of NaCl and BC are not dominant in the atmosphere since they are emitted from totally different places (sea surface vs burning of carbonaceous materials). Mixtures of sulfate, organic aerosol, and nitrate would be more important for the atmospheric implication (e.g., Moffet et al., 2008).

Response: We agree that sulfate and organics are important components of mixed particles containing black carbon. Mixed sulfate/BC and organic/BC particles have been the subject of prior studies, including application of the discrete dipole approximation method (Kahnert et al., 2012). There is also ample evidence of internally mixed NaCl and BC particles to justify our study.

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 the 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 Marine aerosol network.

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

We have modified our manuscript as follows:

On page 2 of the revised paper, the following sentence was added:
"Generally, aerosols are transported far from their source regions and their climatic and environmental impacts are, therefore, delocalized from the source regions. (Kanakidou et al., 2005, Pace et al., 2006 and 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, Smirnov et al, 2011)"

On Page 9 at 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

The mixed particles were obtained from a solution in water. However, the forming process unlikely occur in the atmosphere, and it is probable that the morphologies of the mixed particle differ from those from ambient air. Although most calculations were obtained from the modeled particles, explanations or comparison with other studies that show ambient particle shape of such mixtures are needed

Response: Agreed. As noted in response to Comment #1, we added the following sentence on page 9 of the revised manuscript:

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).

Comment #3

In Fig. 3a, there is almost no difference on MAC at wavelength 550nm, which is the most important for the BC absorption. It seems that this result contradicts much of the discussion in this study. It should be noted that, although there are huge differences for MAC in each particles at wavelength <500 nm (especially around 200 nm), solar radiation is relatively weak at the wavelengths.

Response: Correct, MAC is not highly sensitive to BC aggregate shape when the particle size is significantly smaller than the wavelength (Rayleigh regime). The MAC at 550nm will be more sensitive to aggregate shape for larger BC particles, which may be found in the atmosphere.

To clarify, radiative forcing will be affected from both absorption and scattering properties. The scattering coefficients show strong differences in the studied spectral range that depend on aggregate morphology. As a result, we find that aerosol single scattering albedo is highly sensitive to aggregate morphology.

To clarify, we modified the text with the following sentences on page 8 of the revised manuscript:

“Higher MAC values are found for lacy aggregates compared to more compact structures (compare cases A vs. C and D vs. E)….”

“The SSA values for BC aggregates and the homogeneous sphere (HSA) differ markedly (compare cases D, E and S)”

Also, we added the following text at the end of section 4.1 on page 9 of the revised manuscript:

“It is noteworthy that, for the size of particles here presented, MAC values are sensitive to particle shape only at short wavelengths where incoming solar radiation is weak (due to absorption of the ozone layer). On the other hand, the scattering coefficients are sensitive to particle shape over the full solar spectrum. As a result, aerosol SSA, and thus aerosol radiative forcing, is sensitive to particle shape. Further, SSA is retrieved from remote sensing data, where retrieval approximations make use of homogeneous spherical or spheroidal shape (*Dubovik et al.*, 2006; *Mischenko et al.*, 2000). Given the sensitivity of computed values of SSA to BC shape approximation (sphere or aggregate of spheres) and aggregate porosity (shown in Figure 3b) ambiguities in aerosol composition or mixtures retrieved may be expected."

We also added a sentence in the conclusions:

"iv) Computed SSA values are strongly sensitive to the particle shape approximation (HSA vs. aggregate of spheres) and porosity. Further, computed values of SSA at 550 nm range between 0.18 and 0.27 for lacy and compact aggregates, respectively, in agreement with reported experimental values of ... "

Comment #4

P26413 line 8-14. Simulated particles A to E in Fig. 2 have different monomer sizes and number, fractal shapes, and volumes. Thus, it is difficult to discuss the effects of compactness, monomer sizes, or number of monomers on the optical properties separately. It should be effective to change only one factor and keep other factors unchanged to discuss each effect.

Reply: In Figure 3a,b we show MAC and SSA for a composite of BC aggregates with different porosity, number of monomers and monomers diameters in order to show a range of variability in the optical parameters. The heterogeneity of morphological characteristics are representative of the SEM images analyzed.

In Figure 4a,b, not all the cases presented are comparable between each other, as the reviewer commented. Comparison of the optical properties are discussed for case A vs C, and case D and E vs S, then general conclusions are drawn.

On Page 8 of the revised manuscript, we modified the following sentence to clarify this point:

"Cases A through E correspond to five types of aggregates that vary in compactness (porosity) and number and size of monomers. Case S is a homogeneous sphere approximation (HSA). Optical properties are compared for cases A and C, and cases D, E and S. The compared cases present the same morphological characteristics, but vary in porosity.

Predicted values of MAC are shown in Figure 3a for a composite of aggregates."

We also modified the following sentence on page 8 line 204:
"Higher MAC values are found for lacy aggregates compared to more compact structures (compare cases A vs. C and D vs. E)"

Comment #5

P 26414 line 7-18. The discussion about BC and its coating (effects of BC position and coating) is systematically discussed in Fig 4 by Adachi et al. (2010) using fractal BC particles, and the reference would enhance the discussion. The meaning of L13-14"(i) the larger refractive index of the NaCl surrounding the BC (Bohren, 1986; Flanner et al.,2012)" is unclear, i.e., larger than what?

Reply: Agreed. We modified the sentences on page 10 in the following way:

"Compared to bare BC, the MAC of the mixtures increased because i) BC is surrounded by NaCl, which has a larger refractive index than the surrounding bulk medium (air) …. "

"Additionally, radiation is focused near the center of the particle, enabling further absorption enhancement from inclusions that happen to reside near the center of the composite. Bohren et al. (1986) and Adachi et al. (2010) also discuss the effect of the position of BC in a host material."

Comment #6

P26416 L21-23: "The amplification factors of the MAC, attributed to the mixing state of BC with NaCl, vary between 1.2 and 2.7 and are largely independent of wavelength in the visible spectrum:" Please show more discussion regarding the values of the amplification factor. How is "1.2" obtained? In P26414 L6, there is "2.2-2.7" but not 1.2.

Reply: Thank you for noting this ambiguity. We clarified this text by adding the following sentence on page 9 on the revised manuscript:

"MAC amplification factors (MAC(lambda)mixture/MAC(lambda)bare) increase with increasing embedding of BC in NaCl. For example, an amplification factor of 1.2 is found when the lacy BC aggregate is partially included on NaCl (case FIS), while a value of about 2.2 corresponds to the same lacy BC aggregate completely included in NaCl (case FI). The compactness of the BC aggregate…."

Also, we removed the sentence:
"The maximum MAC amplification factor (about 2.2 - 2.7) is found when BC is completely immersed in NaCl (compare cases FI and GI to cases F and G)"

References:

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