Response to Comments from Anonymous Referee #1

Response to comments on "Understanding the Optical Properties of Ambient Sub- and Supermicron Particulate Matter: Results from the CARES 2010 Field Study in Northern California" by C. D. Cappa et al.

We thank the reviewer for her/his comments, which have helped us to improve our work. The original reviewer comments are in **black** and our responses are in **blue**.

This paper comprehensively reports the results of optical properties measurements made as part of the CARES campaign. This is a very weighty paper and while the conclusions could not really be regarded as game-changing, the high quality of the measurements and the depth of the analysis means that these results are still very important and relevant to ACP, having a wide range of potential applications in radiative transfer and the interpretation of remote sensing data. I would recommend that this be published subject to minor corrections.

General: I found the various combinations of sampling conditions referred to a bit bewildering at times. It would greatly help the reader if a schematic figure could be given showing the different sampling arrangements for the different sites. On a related note, I also found the large number of mathematical symbols to be a bit confusing at times, so it would be useful to compile these as a table.

A table has been added to aid the reader in recalling the definition of symbols used throughout the manuscript (new Table S1). A schematic has also been added to the supplemental material (new Figure S2).

Line 122: The method used to humidify the sample flow to 85%, including the methods to monitor and control the humidity, should be described here.

The following sentence has been added to address the method used for humidification:

"The air stream was humidified by passing it through a custom humidifier, which consisted of a semi-permeable capillary membrane (Accurel) that was kept continuously wetted. The relative humidity in the CRD cells was monitored using Vaisala RH probes (HMP50) that were calibrated using saturated salt solutions."

Line 128: A reference should be supplied for the mobility conversion for the aerodynamic diameters. Rather than assume sphericity (which is probably not valid for dust and dry sea salt particles), it would probably be more correct to refer to the assumed 2 g/cc density as the 'effective' density.

A reference has been added (DeCarlo et al., 2004) and we now use the "effective density" terminology.

Line 138: These mobility diameters should be qualified as 'approximate' because they have each been clearly rounded off compared to the actual theoretical values.

The sentence now reads:

"The mobility equivalent cut-diameters are (assuming a density of 2 g cm^{-3}) *approximately* 700 nm, 1750 nm and 7200 nm, respectively."

Line 166: The factor of 1.66 is contrary to the factor of 1.33 recommended by Laborde et al. (2012b), so the nature of the 'personal communication' cited may need expanding on here.

First, we note that we used 1.53, not 1.66. Second, we note that in Laborde et al., the relationship between Aquadag and Fullerene soot is not 1.33, but a larger factor. From their Fig. 5, using a BC particle mass of 10 fg as a reference point, the scaling between these two is about 1.35/0.9 = 1.5, which is very similar to the value of 1.53 used here. Finally, we have added the sentence "This adjustment factor was determined from laboratory studies conducted after the CARES campaign."

Line 233: A reference should be included here because the exact effect BrC has on AAE is by no means certain.

We fully agree that the effect of BrC on AAE values is "by no means certain." At the same time, it seems quite clear that BrC tends to increase the AAE over pure BC. We have added a reference to Lack and Cappa (2010) here, although there are many references that could be chosen to illustrate this point.

Line 238: Similarly, include references for examples of how SAE is 'commonly used'.

We have added a reference to (Clarke and Kapustin, 2010), which summarizes results from 14 different flight campaigns using SAE as a key criteria for particle size. Many references could be chosen, so we have taken the approach of selecting just one that considers a multitude of different data sets.

Line 384: What AAE would be necessary to cancel out any influence from BrC? How does this compare with DOI:10.1002/2014GL062443?

For BrC to be entirely cancelled out, the AAE for BC would need to simply be assumed equal to the observed AAE, namely 1.17 at T0 and 1.28 at T1 (from Table 2). We have modified the sentence to read: "if the actual AAE_{BC} were >1, as possibly suggested by the $AAE_{532\text{-}660}$ measurements at both sites, then the attributed brown carbon fraction would be even smaller *and cancelled out entirely if* AAE_{BC} *equals the observed value for the ambient particles.*"

Regarding the comparison with Liu et al. (2015), we are not entirely certain what the reviewer is asking us to compare. The Liu et al. (2015) study is primarily a theoretical study when it comes to consideration of the AAE. What we are discussing is really an empirical approach to assessing BrC properties. In other words, an AAE is assumed for BC, and then BrC is "attributed" by difference. Yes, the actual AAE for BC is predicted to be larger than one by Mie theory when "large" particles (~100 nm, as opposed to <30 nm spherules) are used, and as has been discussed many times prior to the Liu et al. study, most notably by Lack and Langridge (Lack and Langridge, 2013) who address specifically the question of how assumptions regarding the AAE of BC influence the attribution of BrC. This is, in some ways, exactly our point in indicating that

if the AAE for BC is > 1 (the base assumption, commonly made) then our attribution would overestimate the absorption attributable to BrC.

Line 402: A more fundamental reason the PALMS and SPLAT II are not capable of quantifying contributions from BC internally mixed on dust particles is the matrix effects associated with each instrument, such that the mass fractions reported on individual particles are not quantitative.

We have modified this sentence to also indicate that matrix effects may preclude explicit quantification even if particles were sampled across the entire size range. Specifically, "Although informative, these measurements unfortunately cannot be used to quantitatively assess the relative contributions of the different absorbing particle types to the supermicron absorption because both instruments sample only over a subset of the entire supermicron size range, e.g. the SPLAT-II only up to $d_{v,a}$ ~ 2 μm, *and matrix effects can impact quantification of individual components in mixed particles (e.g. BC mixed with dust).*"

Line 453: Shouldn't the qualitative influence of sea salt particles be evident in the single particle mass spectrometer data?

Ideally, yes. However the particle sampling statistics during CARES make it difficult to develop a qualitative picture that can be confidently assessed in this case.

Line 514 (and elsewhere): "consistent with that of (Russell et al., 2010)" should read "consistent with that of Russell et al. (2010)"

These have been fixed.

Line 531: This opening statement should be made more descriptive, as it isn't specified what exactly the effect on climate is. It may also be worth mentioning that this is an important parameter for remote sensing retrievals.

The statement now reads:

"The extent to which particles scatter light in the backward versus forward direction has an important controlling influence on their climate impacts, *namely the amount of incident solar radiation that is reflected back to space and the associated radiative forcing* (Haywood and Shine, 1995). *Furthermore, the backscatter fraction and asymmetry parameter are important parameters for remote sensing retrievals.*"

Line 573: Was any correction for thermophoretic losses invoked? If not, the authors should comment on how much of an issue they believe this to be.

Yes, a correction for thermophoretic losses was applied, similar to what was done in Cappa et al. (2012). The correction factor for particles that passed through the TD was 0.8. We have added the following statement to the methods: "Measurements made through the thermodenuder were corrected for thermophoretic losses (Huffman et al., 2008).

Line 593: According to conventional wisdom, supermicron sulphate and nitrate tends to be in the form of salts of calcium and sodium rather than ammonium, which makes them quite involatile, so I would doubt that this is significant.

We have clarified this to indicate that we mean that there could *potentially* be evaporation of "inorganics such as *ammonium* sulfate and *ammonium* nitrate," although we agree with the reviewer that this is likely to be less important than organics.

Line 599: A related hypothesis could be that undenuded sea salt particles do not completely effloresce during drying due to the presence of magnesium salts (doi: 10.5194/acp-15-11273-2015) and organics. If the denuded particles are more completely dried out (due to the water being boiled off) then this would increase their apparent hygroscopicity further.

This is certainly a possibility. The "2-D Area Ratio" reported in the reference given (Gupta et al., 2015) for pure MgCl2 at 30% RH is about 1.3 and for pure NaCl at 80% RH is about 5. Given that the diameter growth factor (GF) for NaCl is ~2 at 80% RH, this implies that the equivalent MgCl2 GF at 30% RH is around 1.07. The mass ratio between Mg and Na in sea water is about 0.12. Thus, the MgCl2 would be only a small fraction of the sea salt (NaCl would dominate) and the MgCl2 would have only a negligible impact on the average water content of the particles. In fact, this is apparent in Gupta et al., who find that the 2-D Area Ratio is only about 1.2 at 30% RH for mixed NaCl/MgCl2 particles where the NaCl mole fraction is 0.9. In this case, the equivalent GF would be 1.05. Thus, although residual water due to magnesium salts could influence the measurements, the magnitude of this influence would be small. Although we believe this to most likely be an unimportant effect, we have added the following sentences to indicate it as a possibility. "It is possible that the thermodenuding removed residual water that did not fully evaporate in the drier due to the presence of magnesium sea salts (which do not effloresce until very low RH), leading to an apparent increase in the hygroscopicity of the thermodenuded particles. However, the potential impact from this is expected to have been quite limited, given the small amount of residual water retained by magnesium salts at low RH (Gupta et al., 2015)."

Line 620: How does this fit in with the conclusions of Doi:10.1038/Ngeo2220?

Saleh et al. (2014) also observe that the brown carbon fraction from biomass burning samples has a higher effective absorptivity at shorter wavelengths. Saleh et al. (2014) also argue that heating can leave behind more lower-volatility organics that are more absorbing than the higher-volatility species that evaporate more easily in a thermodenuder. This can lead to a suppression of observable absorption enhancement values over the "true" value for BC. However, Cappa et al. (2011) showed that the thermodenuder-derived E_{abs} values behaved very similarly to E_{abs} values derived from consideration of mass absorption coefficients for CARES, which suggests that such "residual" more-absorbing organics are playing a negligible role here (see the Supplementary Material of that paper). We also note that Zhang et al. (2016) also found good agreement between thermodenuder-derived and MAC-derived E_{abs} values for a region known to be impacted by biomass burning (the focus of the Saleh et al. study), suggesting that the limitations of the heating method identified by Saleh et al. (2014) may be limited in scope. This is certainly an issue that remains to be fully resolved, but is not a major point of this work and thus we have not pursued it further here.

Line 646: The caveat should be added that this is assuming that the particles have not acquired an involatile coating (e.g. coagulation with sea salt, condensation of humiclike SOA), because this could confound any attempt to isolate the effect of morphological changes on SSA.

We have added the following sentence: "However, if non-absorbing and non-volatile materials remained (e.g. sea salt), then the extrapolated SSA would not be fully representative of pure BC particles, confounding straightforward interpretation in terms of morphological changes."

Line 653: It should be noted that if the particles are thought to be very non-spherical, the SMPS sizing is likely to be overestimated to a large degree

True, but shape effects would not be large enough to make the SMPS-measured 300 nm shift down to < ~50 nm, which would be necessary to explain such small SSA values.

Line 653: If the particles are fundamentally different to 'normal' black carbon particles, then the SP2's calibration could be invalid and the equivalent core sizes reported inaccurate. If the instrument had a narrow band incandescence detector, it may be informative to compare the ratio of this to the broadband detector to see if the apparent colour temperature had changed.

This is an interesting point. Laborde et al. (2012) reported SP2 sensitivities for a variety of different BC types. The largest difference observed corresponded to a sensitivity ratio of about 1.6. If the SP2 were too sensitive towards the asphalt particles by a factor of 1.6 (in per particle mass), then the diameter would be overestimated by a factor of $1.6^{1/3} = 1.17$. Fig. S9 (now S10) showed the particles during the asphalt-impacted period to be about a factor of 2 larger in diameter. This would require a mass sensitivity difference of $2^3 = 8$. This seems unreasonably large, given the results shown in Laborde et al. (2012). Thus, although we agree that the particles may have been detected with a somewhat different sensitivity than typical ambient BC particles, the difference is unlikely to make a substantial impact on the conclusions here, and certainly unlikely to invalidate our conclusion that it is most likely that the particles are composed of smaller spherules.

Figure S1: Adjust the colour scale so that areas covered by land are green rather than blue.

Done.

Figure S9: Given that Babs of black carbon is more closely related to mass than number, a mass-weighted distribution comparison would be informative here.

Done. The conclusions are unaffected.

References

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