Response to Comments from Anonymous Referee #2

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 describes measurements of absorption, scattering, and extinction for PM1, PM2.5, and PM10 particles at two field sites near Sacramento, California. The authors use these measurements to conclude that supermicron particles contribute approximately half of scattering, and are composed of varying amounts of dust and sea salt. Photochemical processing does not have a consistent effect on submicron aerosol scattering, partly due to transport. The authors propose relationships between other intensive aerosol properties. This is a well-written paper, although the discussion is long and could possibly benefit from some condensing. I recommend publication after the following issues are addressed.

Major comments:

1. The introduction is short and does not summarize existing knowledge about the composition and optical properties of supermicron aerosol. A previous study from the CARES campaign has already reported the unexpectedly large contribution of coarse mode aerosol to radiative forcing (Kassianov et al., 2012). This paper and other relevant results (possibly including Malm et al., 1994; Dubovik et al., 2002; Hand et al., 2002; Malm et al., 2007; Eck et al., 2010) should be described and cited in an expanded introduction.

We have expanded the introduction to some extent. We now note that while measurements of PM_1 and PM_{10} composition and mass (which allows determination of supermicron particle properties) have become routine, the measurements of supermicron particle optical properties (via difference between PM_{10} and PM_1 measurements) remain relatively uncommon. This goes directly to studies such as Kassianov et al. (2012), in which optical properties were inferred from size distribution measurements. Our paper reports on actual measurement of the supermicron optical properties and does not rely on "reconstruction" of optical properties from mass or composition measurements. We have added the following to the introduction:

"Measurements of particulate mass concentrations and composition for $PM_{2.5}$ and PM_{10} have become routine through networks such as the U.S. Interagency Monitoring of Protected Visual Environments (IMPROVE) network (Malm et al., 2007), and these can be used to "reconstruct" aerosol optical properties (Malm and Hand, 2007). However, direct measurements of the optical properties of particles between different size regimes are much less common, and where they do exist are quite often made in the marine boundary layer (e.g. Bates et al., 2006) and not over land. ($PM_{2.5}$ and PM_{10} refer to particulate matter with aerodynamic diameters below 2.5 μm and 10 μm, respectively.)"

"A previous analysis of particle size distributions measured during the CARES campaign indicated a large contribution of supermicron aerosol to the total particle scattering (Kassianov et al., 2012). Here, direct measurements of the scattering by these supermicron particles are reported on, and their sources and properties and the factors that drive their variability are examined."

"Results from *in situ* measurements such as here can help to inform remote sensing retrievals and climatologies, which can provide a much broader spatial picture of sub- versus supermicron abundances and contributions to light scattering and extinction (Dubovik et al., 2002; Eck et al., 2010)."

2. Lines 156-157: "Data during the first week of the campaign (June 3-12) are especially noisy due to instrumental problems." What caused the noise and were the measurements still accurate?

The noisy AMS data during the first week occurred because the AMS was inadvertently set wrong during the first week, with a very short MS-open duration and long MS-closed duration. This uneven open/closed cycle was the cause of noisier data (decreased precision) but did not affect quantification. The AMS was returned to normal setting of equal durations for MS open and MS closed mode June 16 onwards.

3. Section 2.2: What were the specific differences between the T0 and T1 site? Were the HR-AMS instruments operated by the same research group? Do the different OOA mass factors represent true aerosol composition differences between the sites?

There are many differences in location, available instrumentation and operators between the T0 and T1 sites. All of these differences are detailed in the "Overview of the 2010 Carbonaceous Aerosols and Radiative Effects Study (CARES)" by Zaveri et al. (2012), which is referenced in the overview of the Experimental section. As specified in Zaveri et al. (2012), the HR-ToF-AMS was operated by Qi Zhang's group from UC Davis at the T1 site and by Chen Song and Rahul Zaveri's group from Pacific Northwest National Laboratory at the T0 site. Regardless, OOA never represents "true" aerosol composition differences, only a mathematical representation of those differences that has some physical/chemical interpretation. However, the reviewer is most likely asking about comparability between OOA from the two sites. The HR-AMS measurements from T0 and T1 are discussed at length in Setyan et al. (2014), and thus rather than repeating those results here, we refer the reader to that work for more details. But the short answer is "yes, the differences in OOA factors are meaningful."

4. Section 3.1: Besides Kassianov et al. (2012), what have prior studies of supermicron aerosol extinction under relatively clean conditions observed?

To be clear, Kassianov et al. (2012) calculated supermicron aerosol extinction from size distributions, while in the current study we actually report on measurements of the scattering, absorption and extinction by the supermicron particles in this region. As we now note in the introduction, direct measurements of supermicron optical properties are fairly uncommon, and where they do exist are most often found for the marine boundary layer where the contribution of sea spray will be large. We have focused our revisions on studies in which optical properties

were measured (either *in situ* or remote sensing) and not considered measurements of particulate mass concentrations alone. To this end, we have added an extensive comparison with some remote sensing results that look at the relationship between Angstrom exponents and the fine mode fraction of extinction, and that look at the relationship between the SSA and the fine mode fraction of extinction. We have added two new figures in support, one in the supplemental and one in the main text.

The added text and figures are provided below.

"Clarke and Kapustin (2010), in a survey of hemispheric aerosol vertical profiles, used a value of $SAE_{450,550} = 1.3$ as a dividing line between air masses impacted by smaller particles from combustion sources ($SAE_{450,550} > 1.3$) or coarse-mode particles, such as sea salt and dust ($SAE_{450,550} < 1.3$). Our results indicate that $SAE_{450,550,PM10} = 1.3$ corresponds to $f_{sca,550,PM1} = 0.50$, suggesting that $SAE_{450,550} = 1.3$ is a reasonable dividing line between sub- and supermicron aerosol. They also observed that the relative magnitudes of scattering by smaller versus larger particles was highly variable, depending on altitude and region."

"However, a better property to compare with remote sensing methods may be the PM_{10} extinction Ångstrom exponent (EAE_{PM10}) versus the PM_1 extinction fraction, $f_{ext,PM1}$. This is complementary to the SAE_{PM10} versus $f_{sca,PM1}$ relationship discussed above, but focuses on the total optical losses (scattering plus absorption) as opposed to just scattering. The EAE_{PM10} and $f_{ext,PM1}$ values (for the various wavelength combinations) also exhibit reasonably linear relationships (Fig. SX). The EAE_{PM10} value when $f_{ext,PM1} = 0.5$ is used here as a reference point (referred to here as EAE_{PM10}-50). For a given EAE_{PM10} wavelength pair the EAE_{PM10}-50 increases notably as the wavelength for $f_{ext,PM1}$ increases, exhibiting much less sensitivity to the choice of wavelength pair (although generally decreasing as the wavelength pairs increase) (Table SX). For example, for $EAE_{450,700,PM10}$ the EAE_{PM10}-50 increases from 0.85 to 1.09 to 1.37 for $f_{ext,PM1,450}$ to $f_{ext,PM1,550}$ to $f_{ext,PM1,700}$. The EAE_{PM10} versus $f_{ext,PM1}$ relationships from these *in situ* measurements can be compared with remote sensing retrievals of the wavelength dependence of the AOD and the "fine mode fraction" (*FMF*) of AOD, which is nominally the same as the $f_{ext,PM1}$ values here. As one example, Eck et al. (2010) investigated the relationship between the *FMF* of AOD and *EAE* from AERONET AOD measurements for a few locations around the world. The Eck et al. (2010) observations suggest $EAE_{440\text{-}870,PM10}$-50 ~ 0.5 at 440 nm and $EAE_{440\text{-}870}$-50 ~ 0.9 at 675 nm. These are somewhat smaller than what is observed here, although given the wavelength differences between the *in situ* and remote sensing measurements the difference is not unreasonable. Some of the difference in the EAE_{PM10}-50 values could be attributable to differences in absorption by non-BC species in the regions studied in Eck et al. (2010) (India, China, West Africa) versus in the Sacramento region."

"The relationship between the PM_{10} *SSA* and the PM_1 fraction of extinction can also be examined to understand how particle size relates to the extent of scattering versus absorption. At T0, the SSA_{PM10} at all three wavelengths decreases as $f_{ext,PM1,700}$ increases for $f_{ext,PM1,700} < 0.7$, at which point the trend reverses and SSA_{PM10} increases with $f_{ext,PM1,700}$. At T1, the relationship is somewhat different, with SSA_{PM10} decreasing with $f_{ext,PM1,700}$ until about $f_{ext,PM1,700} = 0.55$, above which the SSA is relatively constant. The decrease in SSA_{PM10} with $f_{ext,PM1}$ below some value can

be understood as resulting from an increasing contribution of absorbing black carbon as PM_1 comes to dominate the extinction, and limited absorption by the supermicron particles at all wavelengths. The increase at T0 above $f_{ext,PM1,700}$ can be understood as an increase in the contribution of local, photochemical production of secondary inorganic and organic aerosol within the submicron size range. At T1, the flat relationship above $f_{ext,PM,700}$ likely results from a dampening of the local BC impact as air masses travel from T0 to T1. When $f_{ext,PM1,700}$ is small (supermicron dominated) the SSA_{PM10} increases very slightly with wavelength (i.e. $SSA_{PM10,700} > SSA_{PM10,450}$), but as $f_{ext,PM1,700}$ increases the trend is reversed and the differences between wavelengths become larger. This demonstrates that the SSA versus wavelength relationship is fundamentally different between the sub- and supermicron particles in this region. These relationships can also be compared with results from remote sensing, specifically from AERONET (Eck et al., 2010). (Note that SSA from AERONET retrievals are limited to periods when the AOD is > 0.4 at 440 nm, which is generally during high-concentration periods (Dubovik and King, 2000). AERONET AOD measurements (http://aeronet.gsfc.nasa.gov/) are available from the nearby McClellan Air Force Base from June 8-12, 2010, overlapping the CARES study period. During these days, the maximum AOD_{440nm} (for Level 2 data) was ~ 0.20, below the SSA retrieval threshold.) The shape of the observed SSA_{PM10} versus $f_{ext,PM1,700}$ curves at T0 are quite similar to that observed by AERONET for SSA_{675} versus FMF_{675} over India (Kanpur) and China (Beijing). However, the SSA_{440} versus FMF_{675} curves from AERONET over these same locations was much flatter than observed here for $SSA_{PM10,450}$. This could reflect differences in the nature of the supermicron particles between these regions and Sacramento, with apparently higher absorption by supermicron particles at shorter wavelengths in India and China leading to a weaker dependence of SSA_{440} on particle size than observed here."

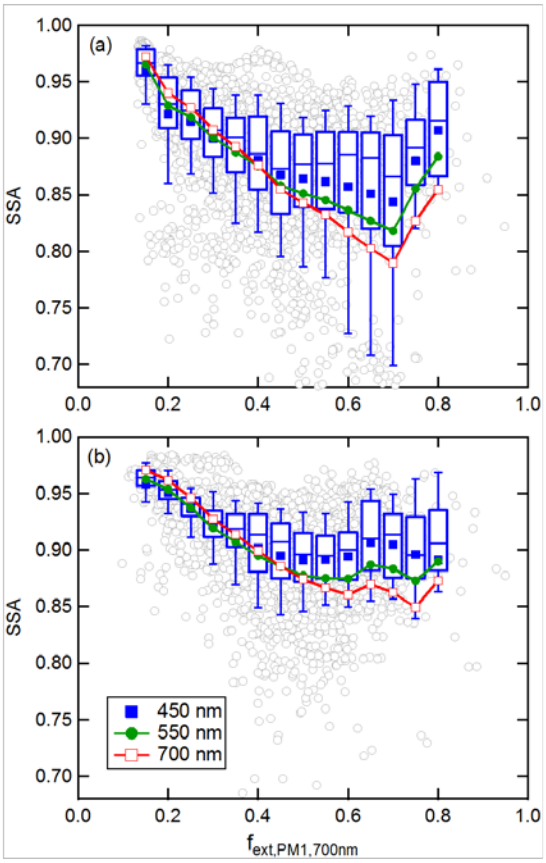

Figure 4. Relationship between the PM_{10} SSA and the PM_1 fraction of extinction at 700 nm, $f_{ext,PM1,700}$, for the (a) T0 and (b) T1 sites. The individual data points (gray, circles) are shown for the SSA_{PM10} at 450 nm along with a box-and-whisker plot binned by $f_{ext,PM1,700}$. For the SSA_{PM10} at 550 nm (green line) and 700 nm (red line) only the mean, binned values are shown.

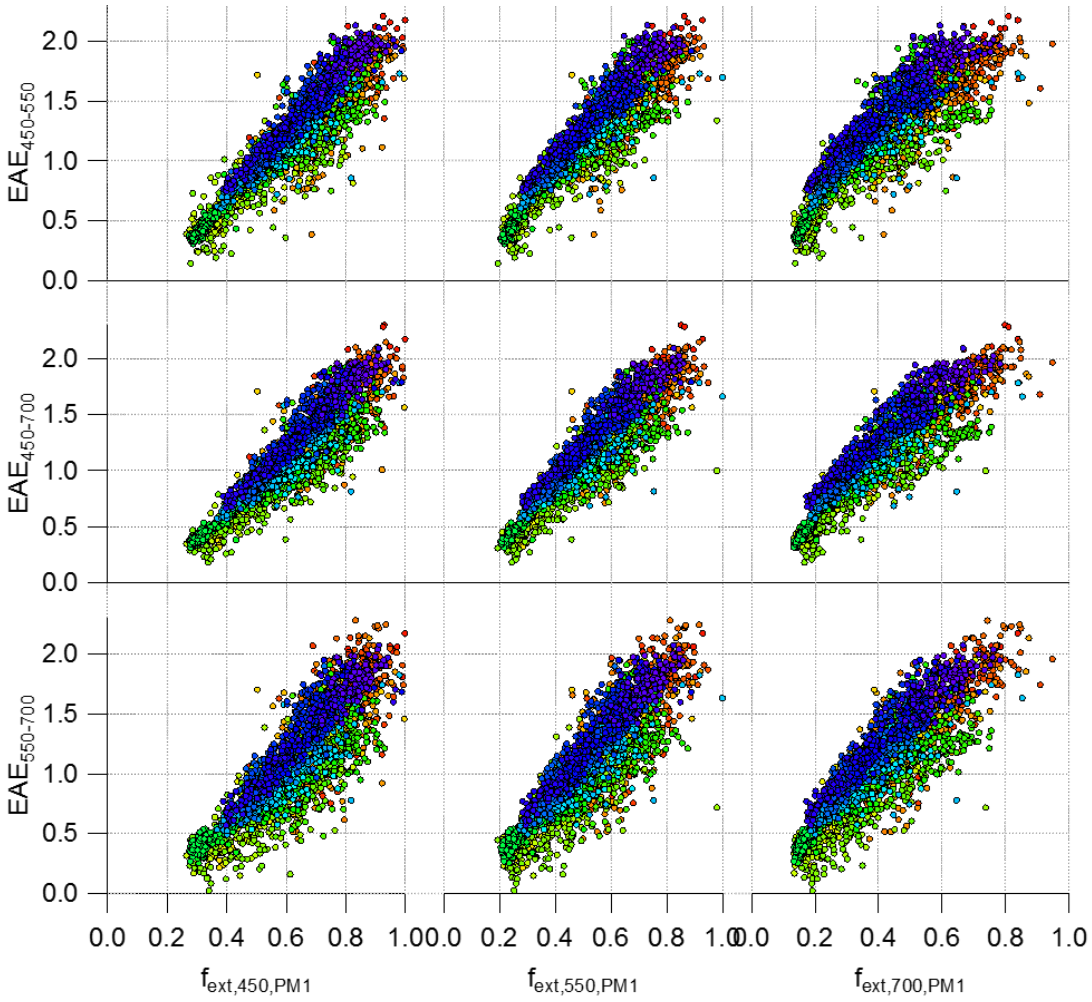

Figure S6. The relationship between the extinction Ångstrom exponent for PM_{10} for different wavelength pairs and the PM_1/PM_{10} scattering ratio at different wavelengths for the T0 site. The points are colored according to time during the campaign, as in Figure S4. The *EAE* values when $f_{ext,PM1} = 0.5$ are reported in Table S3.

Minor comments:

Line 129: Give model and manufacturer for SMPS.

Done.

Line 176: What is the part number of the NOx chemiluminescence instrument?

We now give further information about the operation of the instrument, specifically stating "Gas-phase concentrations of the sum of NO and NO_2 (= NO_x) and the sum of nitrogen oxides (= NO_y) were measured using a 2-channel chemiluminescence instrument (Air Quality Design, Inc, High Performance, 2-Channel) in which NO_2 is photolyzed to NO *using a blue light photolytic converter* and NO_y is converted to NO on a Mo catalyst," and where the new text is in italics.

Typographic corrections:

Line 32: "... but the there is some" - done

Line 79: Use SI units. - done

Lines 99,125, 203, 205: Remove comma after June - done

Line 157: This is a very long week. – We now indicate this is a week and a half

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