Response to Comment on "Radiative Absorption Enhancements Due to the Mixing State of Atmospheric Black Carbon"

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Jacobson argues that our statement that "many climate models may overestimate warming by BC" has not been demonstrated. Jacobson challenges our results on the basis that we have misinterpreted some model results, omitted optical focusing under high relative humidity conditions and by involatile components, and because our measurements consist of only two locations over short atmospheric time periods. We address each of these arguments, acknowledging important issues and clarifying some misconceptions, and stand by our observations. We acknowledge that Jacobson identified one detail in our experimental technique that places an additional constraint on the interpretation of our observations and reduces somewhat the potential consequences of the stated implications.

In Cappa *et al.* (*1*), we explicitly compared observations of ambient black carbon (BC) particle absorption enhancements (E_{abs}) and average mixing states with observationally constrained Mie theory predictions to establish whether core-shell (CS) Mie theory accurately reproduces the observed E_{abs}. Such comparisons are necessary because the ability of theoretical methods to accurately predict BC light absorption depends not only on particle mixing state (i.e., the extent to which BC is internally mixed with other components) but also on particle morphology (i.e., the physical arrangement of the BC with respect to the other components within a given particle). CS Mie theory assumes that internally mixed BC exists as spherical "cores" surrounded concentrically by non-BC "shell" material. Many, although not all, climate models have adopted CS Mie theory to simulate BC optical properties of internal mixtures (*2*). In (*1*), we addressed whether or not observations support this morphology assumption, and we ultimately concluded that (i) CS Mie theory did not accurately reproduce observed E_{abs}, (ii) observed E_{abs} for "thickly coated" and "aged" particles was surprisingly small, and (iii) laboratory observations can give E_{abs} that are consistent with CS Mie theory and that are substantially larger than our field observations. These observations suggest that consideration of mixing state is a necessary, but not sufficient, criterion for establishing whether CS Mie theory is appropriate for use within climate models. The implication of our observations is that many climate models may overestimate the warming influence of BC particles, as many consider internal mixing and use CS Mie theory. Our conclusions and the corollary implication have been challenged by Jacobson (*3*).

Jacobson (*3*) implies that through misinterpretation of the internal processes of some climate models and omissions of several factors or elements, our conclusions about "model error" are invalid. The stated omissions include: (i) our observations were made over short atmospheric times (up to 20 hours of aging) and thereby were "not completely aged"; (ii) our measurements were experimentally controlled under low relative humidity (RH) conditions and thus do not include high RH observations; (iii) thermally denuding particles to ~200°C does not remove involatile material; and (iv) our measurements only took place in two locations and thus are not statistically significant to global climate. We address each of these experimental issues individually, starting with the issue of residual particulate material after denuding.

First, Jacobson suggests that denuding [to the temperatures reported in (*1*) of >175°C and discussed in the supplementary materials, section S1.2.5] will not remove involatile crustal or sea-salt material associated with BC particles due to coagulation or cloud processing. In (*1*), we did not explicitly examine the effects of residual material, such as involatile material, on the measured and calculated optical properties of BC particles. By carefully reexamining the SP-AMS mass spectra, we have now quantitatively characterized the residual particulate material on BC particles after denuding at temperatures >175°C. Jacobson was correct in noting that denuding BC-containing particles at temperatures between 175°C and 250°C [temperatures used in (*1*)] may not remove all non-BC particulate material. Analysis of BC-containing particle residual material using SP-AMS mass spectra indicates a minor contribution due to involatile components such as sea salt. The measured [sea-salt]:[BC] ratio averaged ~1%, which is consistent with filter measurements that indicate the total [sea-salt]:[BC] ratio in submicron particulate matter (PM) is less than 10% (including sea-salt particles without BC). The most substantial component of the residual material is identified as nonrefractory (NR) organic and SO_4^{2-} internally mixed with the BC, which had not been fully removed by our thermal denuding process. The ratio between the total amount of nonrefractory residual material and BC termed (R_{BC} = [NR-PM$_{BC}$]/[BC]) was large enough to substantially influence the calculated E_{abs}, and therefore potentially also the measured E_{abs}. In figure 2 of (*1*), the observed E_{abs}, which includes the influence of the residual non-BC material, were compared with CS Mie calculations that assumed thermally denuded BC particles had no remaining residual material.

We have recalculated the theoretical maximum E_{abs} from CS Mie based on the measured ambient R_{BC} and the measured residual material (residual R_{BC}) after thermal denuding, where core-shell morphologies have been assumed for both cases. The inclusion of this residual material decreases the calculated maximum E_{abs} from the no-residual calculation in (*1*), as shown in Fig. 1. Comparison of the recalculated maximum E_{abs} with the observations indicates that the overestimate of CS Mie theory is still substantial, but only about half of the originally stated ~200% (factor of 2) overestimate suggested in (*1*). Therefore, although the implications of our observations have been partially reduced, our fundamental conclusions do not change; our observations of ambient, internally mixed BC particles suggest that models that assume core-shell configuration (e.g., CS Mie theory) may overestimate the atmospheric warming by BC.

Second, Jacobson suggests that our observed ~20 hours of photochemical aging is insignificant,

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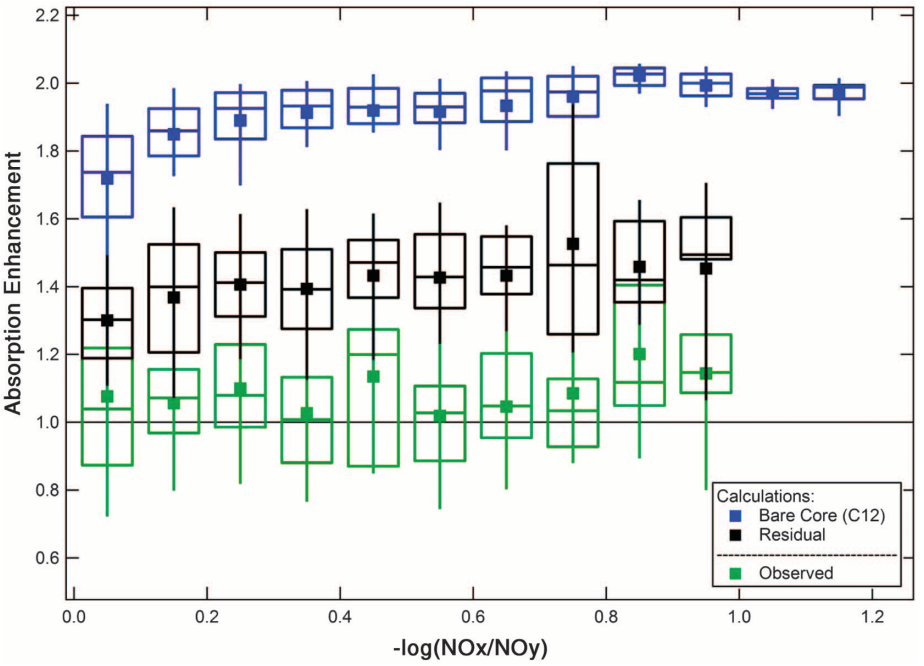

Fig. 1. Observed E_{abs} (green) compared with the theoretical maximum E_{abs}, assuming a bare black carbon core (blue) and the theoretical maximum E_{abs} using the measured residual R_{BC} (black), calculated using CS Mie theory. The box and whisker plots show the mean (■), median (–), lower and upper quartile (boxes), and 9th and 91st percentile (whiskers) results determined from individual measurements.

compared with ~1 week lifetimes for soot particles. We measured the ensemble of airborne BC particles present during CalNex and Carbonaceous Aerosols and Radiative Effects Study (CARES) studies in California and, although the air masses sampled may have been often dominated by local sources with relatively short atmospheric durations, we did not exclude any measurements or particle types within the capabilities of our techniques. We note that 20 hours of photochemical aging corresponds to ~2 days of actual time in regions where OH is the primary oxidant. Also, condensation of photochemically formed secondary particulate material was observed to be rapid [see figure 1A in (*1*)]. We directly measured the mean mixing state and coating/BC ratio of BC particles as they aged in a highly photochemically active environment and used these observations as explicit constraints for our CS Mie calculations; this allowed for direct comparison between the observed and theoretically expected E_{abs}. The extent of photochemical processing is shown in (*1*) to directly correlate with the increase in nonrefractory coating material on the BC particles, providing a physical explanation for the range of coating/BC ratios observed. Our conclusion is that CS Mie theory does not accurately describe the measured ambient E_{abs} values, given the measured coating/BC ratios.

Our measurements were experimentally constrained under low relatively humidity conditions (~55%). Jacobson (*3*) suggested that "high RH" conditions (≥95%) are an important omission in our work. In the context of global climate, we agree that measurements and modeling of high relative humidity conditions may be important and should be conducted. However, RH is a dynamic property that varies dramatically throughout the atmosphere and is most of the time much less than 95% (*4*). Thus, "high RH" conditions represent only a subset of conditions that are important to global climate, and the relative humidity conditions of our measurement conditions are broadly relevant.

Finally, the question raised by Jacobson regarding individual E_{abs} values being <1.0 is addressed in our supplementary materials (section S1.2.5, fig. S6). Briefly, E_{abs} was determined by measuring absorption sequentially in time (ambient, thermally denuded, ambient…), and small, real fluctuations in sampled aerosol optical properties caused the observed fluctuations in E_{abs} measurements. Because average E_{abs} values were unity for the sequential ambient measurements, the small, real fluctuations were observed as variations around unity in the individual E_{abs}.

Furthermore, because these fluctuations are real, they must be included in the average E_{abs} values. We thank Jacobson for his comment and acknowledge that to understand completely the full implications of our observations, it is important that future measurements are expanded to more explicitly consider absorption at higher RH, the effects of residual components after thermal denuding, and to make measurements at more locations and over time. However, these criticisms do not invalidate our observations and conclusion that CS Mie theory may not be appropriate for the simulation of optical properties of ambient BC particles because the (dried) ambient BC particles behaved significantly different from (dry) BC particles that were coated to a similar extent in the laboratory, and also exhibited significantly lower E_{abs} than our observationally constrained calculations. The implications of this are clear: If CS Mie theory is not appropriate for ambient particles—whether only at low RH or at both low and high RH—then climate models that use CS Mie theory may overestimate warming by BC. This would be true both for models that "assume" internal mixing and for those that explicitly calculate mixing states of individual particles [such as Jacobson's Gas, Aerosol, Transport, Radiation, General Circulation Mesoscale and Ocean Model (GATOR-GCMOM) (*5*)], as long as they assume CS configurations.

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