Effect of intrinsic organic carbon on the optical properties of fresh diesel soot

Gabriella Adler^a, Ali Abo Riziq^a, Carynelisa Erlick^b, and Yinon Rudich^{a,1}

^aDepartment of Environmental Sciences, Weizmann Institute, Rehovot 76100, Israel; and ^bDepartment of Atmospheric Sciences, The Hebrew University of Jerusalem, Jerusalem 91904, Israel

Edited by Barbara J. Finlayson-Pitts, University of California, Irvine, CA, and approved October 14, 2009 (received for review March 30, 2009)

This study focuses on the retrieval of the normalized mass absorption cross section (MAC) of soot using theoretical calculations that incorporate new measurements of the optical properties of organic carbon (OC) intrinsic to fresh diesel soot. Intrinsic OC was extracted by water and an organic solvent, and the complex refractive index of the extracted OC was derived at 532 and 355-nm wavelengths using cavity ring-down aerosol spectrometry. The extracted OC was found to absorb weakly in the visible wavelengths and moderately at blue wavelengths. The mass ratio of OC and elemental carbon (EC) in the collected particles was evaluated using a thermo-optical method. The measured EC/OC ratio in the soot exhibited substantial variability from measurement to measurement, ranging between 2 and 5. To test the sensitivity of the MAC to this variability, three different EC/OC ratios (2:1, 1:1, and 1:2) were chosen as representative. Particle size and spherule morphology were estimated using scanning electron microscopy, and the soot was found to be primarily in the form of aggregates with a dominant aggregate diameter mode in the range 200–250 nm. The measured refractive index of the extracted OC was used with a variety of theoretical models to calculate the MAC of internally mixed diesel soot at 532 and 355 nm. We conclude that Rayleigh–Debye–Gans theory on clusters of coated spherules and T-matrix of a solid EC spheroid coated by intrinsic OC are both consistent with previous measurements; however, Rayleigh–Debye–Gans theory provides a more realistic physical model for the calculation

black carbon | cavity ring-down | coated particles | mass absorption cross section

Soot is generated by industrial activities, traffic, fires, and household burning of coal and biomass fuels. Soot particles are highly nonspherical and are composed of agglomerates (Fig. 1). It is the product of incomplete combustion, especially of coal, diesel fuels, and biomass. Diesel engines contribute about 37% of the energy-related “black carbon” (BC) and 16% of the energy-related organic carbon (OC) that is found in soot aerosols (1). BC is the refractory and strong light-absorbing component of soot. It is termed “black carbon having a graphitic microstructure” (2), elemental carbon (EC), or “graphitic carbon,” which refers to the presence of a graphite-like microcrystalline structure. In atmospheric chemistry, EC refers to nonvolatile carbon below a certain temperature, typically about 550 °C (3).

Soot is a major contributor to Earth’s radiative balance. The estimated global climate forcing for soot aerosols from fossil fuel burning ranges from +0.19 to +0.61 W m^{−2}, as compared to CO₂ with an estimated forcing of +1.66 ± 0.17 W m^{−2} (4). However, due to the short atmospheric residence time of aerosols, the strongest effect is regional rather than global; the regional top of the atmosphere radiative forcing can be two to three times larger than the total global average forcing of greenhouse gases (5, 6). BC can affect regional climate by absorbing sunlight and heating the air, influencing large-scale atmospheric circulation and attenuating the hydrological cycle. BC also affects regional climate indirectly by serving as cloud and as ice condensation nuclei, thereby modifying cloud droplet size and cloud lifetime. By heating an aerosol layer and cooling the layers below, soot and

Fig. 1. Scanning electron microscopy (15) images of diesel soot comprised of chains of aggregates of spherules with average size 200–250 nm.

light-absorbing aerosols can change atmospheric convection and suppress shallow cloud formation (7–9). Additionally, BC deposition on ice increases the absorption of solar energy, resulting in more rapid melting of glaciers and polar ice caps (10). To correctly assess the role of soot in regional and global climate, its optical properties must be measured and modeled correctly.

The optical properties of soot particles are principally analyzed in one of two ways: (a) particles are collected on a filter, and the

Author contributions: A.A.R. and Y.R. designed research; G.A., A.A.R., C.E., and Y.R. performed research; and G.A., A.A.R., C.E., and Y.R. wrote the paper.

The authors declare no conflict of interest.

This article is a PNAS Direct Submission.

¹To whom correspondence should be addressed. E-mail: yinon.rudich@weizmann.ac.il.

This article contains supporting information online at www.pnas.org/cgi/content/full/0903311106/DCSupplemental.

absorption is measured using instruments such as the integrating plate (11), integrating sphere (12), laser transmission (13), aethalometer (14), or particle soot absorption photometer (15); or (b) particles are suspended in air, and absorption is measured using techniques such as photoacoustic spectroscopy (16), single-particle soot photometer (17), or by a combination of extinction and scattering measurements (18). At 550 nm, the experimentally determined complex refractive index (RI) obtained from these methods ranges from $n = 1.5 + i0.5$ to $n = 2.67 + i1.3$ (19). Accordingly, the normalized mass absorption cross section [MAC; $\sigma_{\text{abs}}/(\rho V)$, where ρ is the density of the particle material and V is the volume of material in the particle] ranges between 3 and 25 $\text{m}^2 \text{g}^{-1}$. This range results from a number of factors, one of which is the wavelength dependence. Additional uncertainty arises from filter-based optical measurements and the inconsistency in the mass concentration as determined by different methods. The bulk MAC of diesel soot obtained by transmission and photoacoustic absorption methods ranges from 8.28 to 10.8 $\text{m}^2 \text{g}^{-1}$ at 514.5 nm (20).

BC particles are often mixed or coated with organic and inorganic compounds directly upon emission or accumulated by aging (17, 21, 22). The influence of nonabsorbing coatings on the MAC of soot was investigated in a number of previous studies (3, 6, 18, 19, 22–25). It was found that, in general, nonabsorbing coatings enhance the MAC by approximately 30–50% for very small soot particles (size parameter $x = \pi D/\lambda < 0.3$, where D is the particle diameter, and λ is the wavelength) and for thick coatings ($x > 3$) (3, 18, 24, 25). However, such nonabsorbing coatings do not account for the measured MAC over a wide range of particle sizes, nor do they account for the measured MAC for fresh soot, for which very thick coatings are not relevant.

According to Bond and Bergstrom (3), agreement between theoretical calculations of the MAC and the range of measured MAC values for freshly emitted light-absorbing carbon from fossil fuel combustion [$7.5 \pm 1.2 \text{ m}^2 \text{g}^{-1}$ at 550 nm, independent of particle size (3)] has not yet been achieved. Bond et al. (ref. 24, figure 1) showed that the calculated MAC for homogeneous soot spheres with RI of $n = 1.85 + i0.71$ and density $\rho = 1.8 \text{ g cm}^{-3}$ varies from about 5 $\text{m}^2 \text{g}^{-1}$ for radii of approximately 5–25 nm to about 6.8 $\text{m}^2 \text{g}^{-1}$ for the approximately 100-nm resonant radius and decreases steadily to about 2.5 $\text{m}^2 \text{g}^{-1}$ at 250-nm radius. Thus, only near the resonant radius does the MAC calculated for homogeneous soot spheres lie within the bounds of the measured values (24).

In this study, rather than examine the influence of nonabsorbing coatings, we investigate the influence of intrinsic OC (the OC generated from incomplete combustion and from lubrication oil, which condenses onto soot particles as they are emitted) and its absorbing properties on the MAC of diesel soot using a combination of experimental and theoretical methods.

Results and Discussion

RI Measurements by Cavity Ring-Down Aerosol Spectrometry. Aerosols were generated from the water-soluble material (WSM) and organic-soluble material (OSM) extracted from diesel soot, and their complex RIs were retrieved by cavity ring-down aerosol spectrometry (CRD-AS) (26) at visible (532-nm) and blue (355-nm) wavelengths. The retrievals were first validated by measuring the extinction of 300 and 400-nm diameter polystyrene latex (PSL) spheres and comparing the results with Mie theory (227, 28). The PSL extinction efficiencies matched the Mie calculation within 3% and 5%, respectively. The CRD-AS extinction measurements obtained for WSM and OSM at 532 and 355 nm are presented in Fig. 2. The extinction efficiency (Q_{ext}) was measured as a function of particle size parameter (solid circles) and is shown along with the corresponding Mie calculation (solid red line). At 532 nm, the retrieved RIs for OSM, $n = (1.516 \pm 0.004) + i(0.05 \pm 0.02)$, and for WSM,

Fig. 2. The measured extinction efficiency (Q_{ext}) as a function of size parameter (x) of WSM (a) and OSM (b) at 532 nm (Upper) and 355 nm (Lower). The solid curve represents the Mie fit to the experimental data.

$n = (1.549 \pm 0.001) + i(0.044 \pm 0.001)$, are very similar. The imaginary part is relatively low, but higher than previously reported for nonabsorbing coatings, with the OSM having a slightly higher absorption than the WSM. The retrieved RIs of OSM and WSM at 355 nm are $n = (1.51 \pm 0.02) + i(0.11 \pm 0.02)$ and $n = (1.70 \pm 0.02) + i(0.07 \pm 0.01)$, respectively. At this wavelength, the real part for WSM is significantly higher than that of OSM, but the OSM has a higher imaginary part. The standard deviation at 355 nm is larger than that of the 532-nm measurements because the mirror reflectivity decreases and the absorbance increases at shorter wavelengths. Hence, the accuracy of the 355-nm result is limited by the uncertainty in the mirror reflectivity in the UV region.

The RI of intrinsic OC in diesel soot derived in this study shares similarities with previous studies of soot from other sources. Kirchstetter et al. (29) applied a light transmission method to extracts from biomass burning and motor vehicle particles collected on quartz fiber filters and extracted with acetone to measure OC absorption. The imaginary part of the OC RI (k) according to Kirchstetter et al. (29) is 0.045 at 500 nm and 0.03 at 550 nm, whereas our CRD-AS measurements yielded an imaginary RI of 0.044 for WSM and 0.05 for OSM at 532 nm. Similarly, the OC imaginary RI according to Kirchstetter et al. (29) is 0.168 at 350 nm, whereas our CRD-AS method yielded an imaginary RI of 0.11 for OSM and 0.07 for WSM at 355 nm. The higher absorption at the blue wavelength is also consistent with measurements of Gao et al. (30).

EC/OC Measurements. Previous studies have shown that the EC/OC mass ratio in soot from diesel engines is sensitive to external conditions, such as vehicle type, year of production, equivalence ratio, engine load, and driving cycle. In Schauer et al. (31), when a known volume of diluted and cooled diesel truck exhaust was filtered directly, the sample consisted of 30.4% OC and 30.8% EC, that is, an EC/OC mass ratio of about 1:1. However, when a semivolatile organic vapor denuder was introduced to the system, it yielded 30.8% EC and 19.7% OC (31). Using different sampling devices, Heibisch et al. (32) measured an EC/OC mass ratio ranging from 2.22 to 2.77 (mean ratio 2.45 ± 0.19). Kweon et al. (33) reported a strong dependence on vehicle engine load, with the ratio of EC mass to the mass of organic matter (OM; a multiplication of the OC mass by a factor of 1.2) less than 1 for lighter loads and greater than 1 for medium to heavy loads. They found that EC mass increases substantially with an increase in equivalence ratio (ratio of air to fuel), whereas the OM mass decreases almost linearly (33). Lough et al. (34) also found a strong

dependence on vehicle weight, reporting an EC/OC mass ratio of 1.9 ± 0.53 for lighter vehicles and 2.7 ± 0.14 for heavier vehicles. Lough et al. (34) additionally reported a strong dependence on year of vehicle production and on the driving cycle, with an EC/OC mass ratio of 3.5 ± 0.19 for older vehicles and 1.7 ± 0.29 for newer vehicles and a ratio that varies between 0.27 ± 0.14 and 5.5 ± 2.4 for different driving cycles (34).

In the current study, samples of soot aerosols emitted from car exhaust (a Toyota ILX 2004, 2494-cm³ diesel turbo engine, engine idle mode) were examined using ten different filters. The EC/OC mass ratio varied and was highly dependent on external conditions, ranging between 2 and 5, in line with previous studies. Given this, for the purposes of our theoretical calculations, we chose three representative EC/OC mass ratios, 2:1, 1:1, and 2:1, with 1:1 as the default ratio based on previous studies [SI Text for a sensitivity study].

Calculations of the Optical Properties. The main theoretical approaches for calculating the MAC of diesel soot with and without intrinsic OC are described in the SI Text and are divided here into ten implementations (labeled 1–10; see also Fig. 3): Implementation 1 is Mie scattering theory on a homogeneous uncoated EC sphere with radius R_g [similar to Bond et al. (ref. 24, figure 1)] but for 532-nm rather than 550-nm wavelength (this is a reference for all other calculations); implementation 2 is classic Rayleigh–Debye–Gans (RDG) theory on an aggregate of total radius R_g containing pure uncoated EC spherules of 10, 15, or 25-nm radius; implementation 3 is RDG theory on pure EC spherules (same as implementation 2) but with the absorption efficiency calculated using a Mie scattering subroutine; implementation 4 is RDG theory on EC spherules coated by OC as part of an aggregate of total radius R_g , where the spherule radius includes both the EC core and OC coating, that is, the total spherule size remains constant at 10, 15, or 25-nm radius; implementation 5 is RDG theory on EC spherules coated by OC (same as implementation 4), with each 10, 15, or 25-nm core coated by OC according to the chosen EC/OC ratio; implementation 6 is T-matrix method applied to a homogeneous uncoated EC spheroid with an equivalent volume to the sphere in implementation 1; implementation 7 is T-matrix method applied to a spheroid comprised of a mixture of OC and EC with a linear relationship between the effective index of refraction and the EC fill density; implementation 8 is T-matrix method applied to a spheroid comprised of a mixture

of OC and EC using the Bruggeman mixing rule to calculate the effective index of refraction; implementation 9 is T-matrix method applied to an EC spheroid coated by OC with the total volume equivalent radius preserved; and implementation 10 is T-matrix method applied to an EC spheroid coated by OC (same as implementation 9), with the volume equivalent radius EC core coated by OC according to the chosen EC/OC ratio. Approaches 6–10 were implemented with two different aspect ratios (0.5 and 2.0).

A range of sizes for the spherules that comprise soot aggregates have been reported in the literature. While Bond and Bergstrom (3), Petzold et al. (35), Sorensen (36), and Seinfeld (37) report spherule radii in the range 2.5–25 nm, Lammel and Novakov (38) report spherule radii of 40–74 nm, and Fuller et al. (19) infer a spherule radius of 60 nm. Based on this and our own SEM measurements of the particles collected on Si wafers (Fig. 1), for approaches 1–5, we assumed a spherule radius of 25 nm. However, we also performed calculations assuming a spherule radius of 10 and 15 nm to test the sensitivity of our results to spherule radius (Fig. S1). In the calculations, the number of spherules was determined by

$$N_{\text{spherule}} = k_f \left(\frac{R_g}{R_{\text{spherule}}} \right)^{D_f}, \quad [1]$$

where $k_f \sim 1.3$ (36), and the fractal dimension $D_f = 1.80$ (36). We varied the total soot size from $R_g = 50$ nm to $R_g = 250$ nm, based on Bond et al. (ref. 24, figure 1); for consistency, the same R_g was used as the radius of gyration in the application of RDG theory (approaches 1–5) and as the volume equivalent radius of the spheroid in approaches 6–10.

Two sets of RI values for EC in the visible (532 nm) were tested: $n = 1.85 + i0.71$ and $n = 1.95 + i0.79$ (3, 24). Due to lack of more information, these two sets were applied in the calculations at 355 nm as well. Higher literature values (ref. 19, table 1) are relevant to condensed graphite without voids (which is not the case for EC emitted from a diesel engine) and were not tested here. For OC, we used our retrieved RI values, where, based on roughly weighing the collected and dried samples, OSM was estimated to compose about 90% of the OC fraction by volume, and WSM was assumed to compose the remaining 10%. The effective total RI of OC, computed using the Maxwell–Garnett mixing rule (39, 40), was $n = 1.519 + i0.048$ at 532 nm

Fig. 3. A representative scheme of the different particle coatings and morphologies used in the theoretical calculations of the normalized mass absorption cross section. Colored numbers at the *Bottom Right* indicate specific models described in the text.

and $n = 1.527 + 0.108i$ at 355 nm. We used an EC density, ρ_{EC} , of 1.8 g cm^{-3} and tested two OC densities, ρ_{OC} , 1.3 g cm^{-3} and 1.5 g cm^{-3} (24, 41).

There is a slight ambiguity in the definition of the MAC regarding the mass by which the absorption cross section is normalized. Whereas it is possible to divide by the total soot mass [$\text{MAC} = \sigma_{\text{abs}}/(\rho_{EC}V_{EC} + \rho_{OC}V_{OC})$], previous studies have essentially typically divided by the mass of elemental carbon only [$\text{MAC} = \sigma_{\text{abs}}/(\rho_{EC}V_{EC})$] (3, 19, 23, 42). To be consistent with these previous studies, we also use the formula $\text{MAC} = \sigma_{\text{abs}}/(\rho_{EC}V_{EC})$.

MAC values derived by computational approaches 1, 2, 4–6, and 9 at 532 and 355-nm wavelengths are presented in Table 1 for the representative size of $R_g = 100 \text{ nm}$ (diameter $D = 200 \text{ nm}$), consistent with our SEM measurements (Fig. 1). Values for both sets of RI for EC and two values of ρ_{OC} are shown. From Table 1, the OC density does not affect the calculated MAC significantly. However, the higher RI for EC ($n = 1.95 + i0.79$) leads to consistently higher MAC values than the lower value ($n = 1.85 + i0.71$). In addition, the MAC is consistently higher at 355 nm than at 532 nm, and the influence of the morphology on the calculated MAC is stronger at the shorter wavelength as well. Comparing with Bond and Bergstrom (3), our calculations suggest that computational approaches 4 and 5 (RDG theory applied to coated spherules) provide the best agreement with the range of measured MAC values at visible wavelengths for all soot size ranges. The derived MAC value at 532 nm (using RI EC $n = 1.85 + i0.71$, RI OC $n = 1.519 + i0.048$, $\rho_{EC} = 1.8 \text{ g cm}^{-3}$, $\rho_{OC} = 1.3 \text{ g cm}^{-3}$, EC/OC ratio 1:1, and spherule radius 25 nm) for coated spherules (approach 4) is $6.8 \text{ m}^2 \text{ g}^{-1}$. For coated spherules where the coating adds to the spherule size (approach 5), the derived MAC value is $7.1 \text{ m}^2 \text{ g}^{-1}$. The derived MAC value at 355 nm (using RI EC $n = 1.85 + i0.71$, RI OC $n = 1.527 + i0.108$, $\rho_{EC} = 1.8 \text{ g cm}^{-3}$, $\rho_{OC} = 1.3 \text{ g cm}^{-3}$, EC/OC ratio 1:1, and spherule radius 25 nm) for coated spherules (approach 4) is $12.2 \text{ m}^2 \text{ g}^{-1}$. For coated spherules where the coating adds to the spherule size (approach 5), the derived MAC value is $13.3 \text{ m}^2 \text{ g}^{-1}$. A complete sensitivity study varying the EC RI, OC density, EC/OC ratio, and spherule size is presented in Fig. S1.

The agreement of RDG theory on coated spherules (using RI EC $n = 1.85 + i0.71$, $\rho_{EC} = 1.8 \text{ g cm}^{-3}$, $\rho_{OC} = 1.3 \text{ g cm}^{-3}$, and EC/OC ratio 1:1) with the MAC recommended by Bond and Bergstrom (3) is clearly shown in Fig. 4. Whereas the calculations of Bond et al. (24), our similar calculation for homogeneous spheres (model 1, open squares), and the T-matrix method applied to homogeneous spheroids (model 6, green diamond) are all in the range of measured values near the resonant diameter of 200 nm, only RDG theory on coated spherules (model 4, red squares, and model 5, magenta squares) lies within the range of measured values over the entire range of particle sizes. This is because the use of an ensemble of spherules preserves the same surface-to-volume ratio, and hence thickness of the coating,

as opposed to a spheroid, in which the coating thickness changes as a function of size. Having said that, we cannot rule out T-matrix method applied to an EC spheroid coated by intrinsic OC with the total volume equivalent radius preserved (model 9, blue triangles). Though this model overestimates the MAC near the resonant diameter and underestimates the MAC at the largest diameters, it covers a large portion of the range of measured values. Such a model is consistent with some amount of restructuring/compacting of the spherule cluster during mixing with the OC (42).

We conclude that among all of the computational approaches, RDG theory applied to spherules coated with intrinsic OC provides the best agreement with the range of reported measurements of absorption of visible light by soot in Bond and Bergstrom (3). If this description of the microscopic configuration of fresh soot is the most realistic, it represents a unique line of thinking for calculations of aerosol optical properties in atmospheric radiative transfer models. In climate models, rather than internally and externally mixed spheres or coated spheres, the soot component of atmospheric aerosols should be modeled as a set of aggregates of coated spherules, at least for relatively fresh diesel soot. Note that we obtained this agreement with reported measurements using conservative estimates of the EC RI.

The enhancement in absorption due to organic coatings on EC particles has been discussed in several previous theoretical studies and has been observed in laboratory and field experiments (17, 24, 42–45). However, in this study, the measured properties of absorbing intrinsic OC, rather than nonabsorbing species that have accumulated due to aging and cloud processing, have been investigated.

Conclusions

In this study, we investigated the absorption of fresh soot particles emitted from diesel car exhaust and the effect of the presence of intrinsic OC on soot absorption in the visible and blue wavelength regions. The mass ratio of EC to OC, the size and morphology of the soot particles, and the RIs of OC extracted from the soot particles were measured by a variety of methods. These results were incorporated in a sequence of different theoretical models of scattering by nonspherical particles. A challenge concerning most soot measurements is the particles' morphology; we overcame this problem by separating the intrinsic OC from the EC, generating spherical OC particles, and retrieving the OC complex RI using CRD-AS and Mie scattering theory for homogeneous spheres. As a result, the optical properties of intrinsic OC were accurately determined.

The theoretical model that provided the best agreement with previous measurements of absorption by soot for all sizes is RDG theory applied to aggregates of EC spherules individually coated with intrinsic OC. At 532 nm, this approach yielded a MAC value of $6.8 \text{ m}^2 \text{ g}^{-1}$ for EC spherules of 25-nm radius coated by OC, with the size of the spherules and of the total soot particle preserved (approach 4) and a MAC value of $7.1 \text{ m}^2 \text{ g}^{-1}$ for EC

Table 1. Normalized mass absorption cross section (MAC; $\text{m}^2 \text{ g}^{-1}$) at 532 and 355-nm wavelengths calculated for diesel soot particles with $R_g = 100 \text{ nm}$; EC/OC mass ratio 1:1; spherule radius 25 nm; densities $\rho_{EC} = 1.8 \text{ g cm}^{-3}$, $\rho_{OC} = 1.5 \text{ g cm}^{-3}$, and $\rho_{OC} = 1.3 \text{ g cm}^{-3}$; and two different EC RIs (24, 41)

Model	532 nm				355 nm			
	$\rho_{OC} = 1.3 \text{ g cm}^{-3}$		$\rho_{OC} = 1.5 \text{ g cm}^{-3}$		$\rho_{OC} = 1.3 \text{ g cm}^{-3}$		$\rho_{OC} = 1.5 \text{ g cm}^{-3}$	
	1.85 + i0.71	1.95 + i0.79	1.85 + i0.71	1.95 + i0.79	1.85 + i0.71	1.95 + i0.79	1.85 + i0.71	1.95 + i0.79
1	6.44	6.74	6.44	6.74	6.71	6.82	6.71	6.82
2	4.98	5.01	4.98	5.01	7.47	7.51	7.47	7.51
4	6.76	7.02	6.63	6.88	12.15	12.66	11.77	12.26
5	7.12	7.43	6.94	7.23	13.27	13.95	12.73	13.38
6	6.46	6.81	6.46	6.81	6.96	7.08	6.96	7.08
9	8.92	9.63	8.66	9.34	12.05	12.48	11.47	11.86

Fig. 4. Normalized mass absorption cross section at 532-nm (a,b, and c) and 355-nm (d,e, and f) wavelengths as a function of total soot particle diameter for three different spherule radii: 10 nm (a and d), 15 nm (b and e), and 25 nm (c and f) obtained using models 1 (open square), 2 (black square), 4 (red square), 5 (magenta square), 6 (green diamond), and 9 (blue triangle). The EC/OC mass ratio is 1:1, the EC RI is $1.85 + 0.71i$, $\rho_{EC} = 1.8 \text{ g cm}^{-3}$, and $\rho_{OC} = 1.3 \text{ g cm}^{-3}$. The shaded area represents the range of measured values of the MAC for particles comprised of light-absorbing carbon from freshly emitted fossil fuel combustion aerosols at 550-nm wavelength suggested in the recent Bond and Bergstrom review (3) ($7.5 \pm 1.2 \text{ m}^2 \text{ g}^{-1}$). The box highlights results for 25-nm spherule radius, which is the most likely radius according to our SEM measurements and provides the best agreement with previous studies. Note the range of scale in the y-axis.

spherules of 25-nm radius core coated by additional OC and accommodating the additional OC according to EC/OC mass ratio 1:1 (based on previous studies) (approach 5). A solid EC spheroid coated by intrinsic OC with the total volume equivalent radius preserved (approach 9), consistent with some measure of compacting of the cluster during mixing with OC, also provides a plausible model within the estimated uncertainty in the calculations.

We also present the accurate calculations of the MAC of diesel soot with intrinsic OC at ultraviolet wavelengths. At 355 nm, the MAC calculated with approach 4 is $12.2 \text{ m}^2 \text{ g}^{-1}$, whereas the MAC calculated with approach 5 is $13.3 \text{ m}^2 \text{ g}^{-1}$. The higher MAC value in the UV than in the visible is attributed to the stronger absorbance in the UV by intrinsic OC. A limitation of our approach is that the RI of EC was taken from the literature, though we showed that even relatively conservative estimates for the proper RI of EC provide satisfactory results.

Methods

Collection, Sampling, and Extraction. Soot aerosols from a 2494-cm³ diesel engine were collected. Part of the exhaust pipe output was collected in water ($\Omega > 18.3 \text{ Mohm/cm}$) at room temperature, and part was collected by a MOUDI sampler (Model 110 with rotator) for the microscopy and EC/OC measurements. Water-soluble and organic-soluble organics were extracted from the soot collected in the water container. WSM was filtered through a membrane (47 mm, with a cutoff at $0.45 \mu\text{m}$). To extract the OSM, the filter with the precipitate was extracted for a second time with water (18 h on a shaker), immersed in 100 mL of dichloromethane (HPLC grade), and shaken for another 18 h. The organics in the dichloromethane layer were filtered through a crodisc CR 25-mm syringe filter with a $0.2\text{-}\mu\text{m}$ PTFE membrane and dried in a hood. For the CRD measurements, the dried OSM solution was dissolved in a mixture of 1:1 methanol and ethanol.

Aerosol Generation and Selection. Spherical aerosol particles were generated from the WSM and OSM solutions using a constant output atomizer. The droplets were dried in a silica gel column (relative humidity <3%) and neutralized to obtain an equilibrium charge distribution. Solvents were removed using a thermal denuder, consisting of a heated (100°C) copper pipe (64 cm) connected to an activated carbon denuder that adsorbs methanol and ethanol vapors. Following the denuder, size selection of the aerosol was obtained using differential mobility analyzer (46) operating with 4.7 standard liter per minute (SLM) sheath flow and 0.47 SLM sample flow. The resulting aerosols were examined by a CRD aerosol spectrometer with a total flow through the cell of 0.8 SLM.

EC/OC Ratio Measurements. The organic to elemental carbon (EC/OC) ratio of the particles collected by MOUDI was measured using a Sunset Laboratory EC/OC aerosol analyzer (NIOSH 5040) (47, 48).

Aerosol Extinction and Complex Refractive Index Measurements by CRD-AS.

Aerosol extinction at 532 and 355-nm wavelengths was measured by a CRD-AS system, described previously (26, 49). The laser intensity exiting the cavity (93-cm length) is measured with a photomultiplier, and the resulting signal is fed into a digital oscilloscope. The digitized data for each laser pulse is transferred and stored in a computer. The decay time of the laser pulse in an empty cavity is $30 \mu\text{s}$ at 532 nm, corresponding to a mirror reflectivity of 99.988% and to a detection limit of $\alpha_{\min} = 1 \times 10^{-9} \text{ cm}^{-1}$ at a repetition rate of 10 Hz averaged over 100 s. At 355 nm, the decay time for an empty cavity is $3.7 \mu\text{s}$ at 355 nm, corresponding to a reflectivity of 99.91% and to an extinction coefficient of $\alpha_{\min} = 6.7 \times 10^{-8} \text{ cm}^{-1}$ at a repetition rate of 10 Hz over 100 s. The ability to precisely measure minimal differences in ring-down times between an empty cavity (τ_0) and a cavity filled with aerosols (τ) provides a good estimate of the maximum sensitivity.

The aerosol flow enters the cavity through four tubes, designed to ensure good mixing and uniform concentration of the particles throughout the

cavity (26, 50) and exits through a similar configuration. A small purge flow of dry particle-free nitrogen in front of each mirror prevents particle deposition on the mirrors. The resulting dilution is taken into account. The length of the cavity occupied by particles is 68 cm, as determined by precise mechanical measurement. This measurement can introduce about 0.7% uncertainty in the measured extinction. The particle concentration is determined by a condensation particle counter connected at the cavity exit. Only the mode size of the injected aerosol is used in the calculations. Mie curves and RIs

are obtained using a retrieval algorithm for single component homogeneous spherical particles described previously (27).

ACKNOWLEDGMENTS. C.E. thanks A. Moroz for providing the absorbing coated spheroid code and for ongoing consultation on use of the code. The authors thank Mary K. Gilles for insightful discussions. This work was partially supported by the Israel Science Foundation (Grants 1527/07 and 196/08). Y.R. acknowledges financial support by the Helen and Martin Kimmel Award for Innovative Investigation.

- Bond TC, et al. (2004) A technology-based global inventory of black and organic carbon emissions from combustion. *J Geophys Res*, 109:D14203–10.1029/2003JD003697.
- Novakov T (1984) The role of soot and primary oxidants in atmospheric chemistry. *Sci Total Environ*, 36(Jun):1–10.
- Bond TC, Bergstrom RW (2006) Light absorption by carbonaceous particles: An investigative review. *Aerosol Sci Technol*, 40(1):27–67.
- Solomon S, et al. (2007) *The Physical Science Basis. Contribution of Working Group I to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change* (Cambridge Univ Press, Cambridge, New York).
- Ramanathan V, Crutzen PJ, Kiehl JT, Rosenfeld D (2001) Aerosols, climate, and the hydrological cycle. *Science*, 294(5549):2119–2124.
- Jacobson MZ (2001) Strong radiative heating due to the mixing state of black carbon in atmospheric aerosols. *Nature*, 409(6821):695–697.
- Menon S, Hansen J, Nazarenko L, Luo YF (2002) Climate effects of black carbon aerosols in China and India. *Science*, 297(5590):2250–2253.
- Ramanathan V, et al. (2007) Warming trends in Asia amplified by brown cloud solar absorption. *Nature*, 448(7153):575–575.
- Koren I, Martins JV, Remer LA, Afargan H (2008) Smoke invigoration versus inhibition of clouds over the Amazon. *Science*, 321(5891):946–949.
- Hansen J, Nazarenko L (2004) Soot climate forcing via snow and ice albedos. *Proc Natl Acad Sci USA*, 101(2):423–428.
- Horvath H (1993) Atmospheric light-absorption—A review. *Atmos Environ Gen Top*, 27(3):293–317.
- Heintzenberg J, Charlson RJ (1996) Design and applications of the integrating nephelometer: A review. *J Atmos Ocean Technol*, 13(5):987–1000.
- Sadler M, Charlson RJ, Rosen H, Novakov T (1981) An intercomparison of the integrating plate and the laser transmission methods for determination of aerosol absorption-coefficients. *Atmos Environ*, 15(7):1265–1268.
- Hansen ADA, Rosen H, Novakov T (1984) The Aethalometer—An instrument for the real-time measurement of optical-absorption by aerosol-particles. *Sci Total Environ*, 36(Jun):191–196.
- Bond TC, et al. (1999) Light absorption by primary particle emissions from a lignite burning plant. *Environ Sci Technol*, 33(21):3887–3891.
- Moosmuller H, Arnott WP, Rogers CF (1997) Methods for real-time, in situ measurement of aerosol light absorption. *J Air Waste Manage Assoc*, 47(2):157–166.
- Schwarz JP (2008) Coatings and their enhancement of black carbon light absorption in the tropical atmosphere. *J Geophys Res*, 113:D03203 10.1029/2007JD009042.
- Khalizov AF, Xue HX, Wang L, Zheng J, Zhang RY (2009) Enhanced light absorption and scattering by carbon soot aerosol internally mixed with sulfuric acid. *J Phys Chem A*, 113(6):1066–1074.
- Fuller KA, Malm WC, Kreidenweis SM (1999) Effects of mixing on extinction by carbonaceous particles. *J Geophys Res*, 104(D13):15941–15954.
- Marley NA, et al. (2001) An empirical method for the determination of the complex refractive index of size-fractionated atmospheric aerosols for radiative transfer calculations. *Aerosol Sci Technol*, 34(6):535–549.
- Jacobson MZ (2000) A physically-based treatment of elemental carbon optics: Implications for global direct forcing of aerosols. *Geophys Res Lett*, 27(2):217–220.
- Shiraiva M, et al. (2008) Radiative impact of mixing state of black carbon aerosol in Asian outflow. *J Geophys Res*, 113:D24210 10.1029/2008JD010546.
- Chylek P, Ramaswamy V, Cheng RJ (1984) Effect of graphitic carbon on the albedo of clouds. *J Atmos Sci*, 41(21):3076–3084.
- Bond TC, Habib G, Bergstrom RW (2006) Limitations in the enhancement of visible light absorption due to mixing state. *J Geophys Res*, 111(D20):D20211.
- Schnaiter M, et al. (2003) UV-VIS-NIR spectral optical properties of soot and soot-containing aerosols. *J Aerosol Sci*, 34(10):1421–1444.
- Riziq AA, Erlick C, Dinar E, Rudich Y (2007) Optical properties of absorbing and non-absorbing aerosols retrieved by cavity ring down (CRD) spectroscopy. *Atmos Chem Phys*, 7(6):1523–1536.
- Riziq AA, Erlick C, Dinar E, Rudich Y (2007) Optical properties of absorbing and non-absorbing aerosols retrieved by cavity ring down (CRD) spectroscopy. *Atmos Chem Phys*, 7(6):1523–1536.
- Baynard T (2007) Design and application of a pulsed cavity ring-down aerosol extinction spectrometer for field measurements. *Aerosol Sci Technol*, 41(4):447–462.
- Kirchstetter TW, Novakov T, Hobbs PV (2004) Evidence that the spectral dependence of light absorption by aerosols is affected by organic carbon. *J Geophys Res*, 109(D21):D21208 10.1029/2004JD004999.
- Gao RS, et al. (2008) Calculations of solar shortwave heating rates due to black carbon and ozone absorption using in situ measurements. *J Geophys Res*, 113(D14):D14203 10.1029/2007JD009358.
- Schauer JJ, Kleeman MJ, Cass GR, Simoneit BRT (1999) Measurement of emissions from air pollution sources. 2. C-1 through C-30 organic compounds from medium duty diesel trucks. *Environ Sci Technol*, 33(10):1578–1587.
- Hebisch R, et al. (2003) Sampling and analysis of carbon in diesel exhaust particulates—An international comparison. *Int Arch Occup Environ Health*, 76(2):137–142.
- Chol-Bum Kweon DEF, Schauer James J, Okada Shusuke (2002) Detailed chemical composition and particle size assessment of diesel engine exhaust. (Society of Automotive Engineers, Washington, DC) SAE Technical Paper Series 2002-01-2670.
- Lough GC, et al. (2007) Development of molecular marker source profiles for emissions from on-road gasoline and diesel vehicle fleets. *J Air Waste Manage Assoc*, 57(10):1190–1199.
- Petzold A, Kopp C, Niessner R (1997) The dependence of the specific attenuation cross-section on black carbon mass fraction and particle size. *Atmos Environ*, 31(5):661–672.
- Sorensen CM (2001) Light scattering by fractal aggregates: A review. *Aerosol Sci Technol*, 35(2):648–687.
- Seinfeld JH (2004) Air pollution: A half century of progress. *AIChE J*, 50(6):1096–1108.
- Lammel G, Novakov T (1995) Water nucleation properties of carbon-black and diesel soot particles. *Atmos Environ*, 29(7):813–823.
- Chylek P, Videen G, Geldart DJW, Dobbie JS, Tso HCW (2000) Effective medium approximations for heterogeneous particles. *Light Scattering by Nonspherical Particles: Theory, Measurements, and Applications*, ed Mishchenko MI (Academic, New York), pp 273–308.
- Erlick C (2006) Effective refractive indices of water and sulfate drops containing absorbing inclusions. *J Atmos Sci*, 63(2):754–763.
- Dinar E, Mentel TF, Rudich Y (2006) The density of humic acids and humic like substances (HULIS) from fresh and aged wood burning and pollution aerosol particles. *Atmos Chem Phys*, 6:5213–5224.
- Schnaiter M, et al. (2005) Absorption amplification of black carbon internally mixed with secondary organic aerosol. *J Geophys Res*, 110(D19):D19204 10.1029/2005JD006046.
- Jacobson MZ (2006) Effects of externally-through-internally-mixed soot inclusions within clouds and precipitation on global climate. *J Phys Chem A*, 110(21):6860–6873.
- Mikhailov EF, Vlasenko SS, Podgorny IA, Ramanathan V, Corrigan CE (2006) Optical properties of soot-water drop agglomerates: An experimental study. *J Geophys Res*, 111(D7):D07209 10.1029/2005JD006389.
- Lesins G, Chylek P, Lohmann U (2002) A study of internal and external mixing scenarios and its effect on aerosol optical properties and direct radiative forcing. *J Geophys Res*, 107(D10):4094 10.1029/2001JD000973.
- Friedman SP (1998) A saturation degree-dependent composite spheres model for describing the effective dielectric constant of unsaturated porous media. *Water Resour Res*, 34(11):2949–2961.
- Schauer JJ, et al. (2003) ACE-Asia intercomparison of a thermal-optical method for the determination of particle-phase organic and elemental carbon. *Environ Sci Technol*, 37(5):993–1001.
- Birch ME, Cary RA (1996) Elemental carbon-based method for monitoring occupational exposures to particulate diesel exhaust. *Aerosol Sci Technol*, 25(3):221–241.
- Dinar E, et al. (2008) The complex refractive index of atmospheric and model humic-like substances (HULIS) retrieved by a cavity ring down aerosol spectrometer (CRD-AS). *Faraday Discuss*, 137:279–295.
- Pettersson A, Lovejoy ER, Brock CA, Brown SS, Ravishankara AR (2004) Measurement of aerosol optical extinction at 532nm with pulsed cavity ring down spectroscopy. *J Aerosol Sci*, 35(8):995–1011.