Markedly enhanced absorption and direct radiative forcing of black carbon under polluted urban environments


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Abstract

Black carbon (BC) exerts profound impacts on air quality and climate because of its high absorption cross-section over a broad range of electromagnetic spectra, but the current results on absorption enhancement of BC particles during atmospheric aging remain conflicting. Here, we quantified the aging and variation in the optical properties of BC particles under ambient conditions in Beijing, China, and Houston, United States, using a novel environmental chamber approach. BC aging exhibits two distinct stages, i.e., initial transformation from a fractal to spherical morphology with little absorption variation and subsequent growth of fully compact particles with a large absorption enhancement. The timescales to achieve complete morphology modification and an absorption amplification factor of 2.4 for BC particles are estimated to be 2.3 h and 4.6 h, respectively, in Beijing, compared with 9 h and 18 h, respectively, in Houston. Our findings indicate that BC under polluted urban environments could play an essential role in pollution development and contribute importantly to large positive radiative forcing. The variation in direct radiative forcing is dependent on the rate and timescale of BC aging with a clear distinction between urban cities in developed and developing countries. We suggest that mediation in BC emissions achieves a co-benefit in simultaneously controlling air pollution and protecting climate, especially for developing countries.


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PNAS Early Edition | 1 of 6
During our experiments were 36 particles with a diameter smaller than 2.5 μm (i.e., <2.5 μm) in Houston (19). In addition to anthropogenic volatile organic compounds (VOCs), noticeable organic and inorganic (i.e., sulfate and nitrate) species to the particle mass concentrations have been found to decrease and increase throughout the pollution period in Beijing (18). The contributions of organic and inorganic species to the total coating thickness equals half of the initial mass equivalent diameter (Dme,0) for the three particle sizes, corresponding to a coating fraction (ΔDme/Dme,0) of 0.5.

**Photochemical Aging of BC Particles.** Distinct BC aging in Beijing and Houston. Temporal variation in the BC mass equivalent diameter (ΔDme or total coating thickness) as a function of exposure time to ambient air in Beijing (A) and Houston (B). The yellow, blue, and red symbols in A represent experiments conducted with the initial BC mobility diameters (Dmob) of about 100 nm, 150 nm, and 220 nm, respectively. The green symbols in B represent experiments conducted with the initial mobility diameter of about 100 nm. The symbols denote measurements conducted on different days, and the dashed lines connect the measurements of the same experiments.

Our measurements demonstrate that the BC morphology variation during atmospheric aging is characterized by two distinct stages, which are delineated by the coating fraction or DSF, i.e., the initial conversion from a highly fractal structure to a spherical shape with the coating fraction <0.5 or DSF >1 and the subsequent growth of the fully compact particles with the coating fraction >0.5 or DSF ≈1 (Fig. 4). For fractal BC particles, there is negligible absorption variation, whereas compact BC particles exhibit noticeably enhanced MAC, with the maximum absorption enhancement factor of 2.4 for a coating fraction of unity. BC particles undergo rapid morphology modification in Beijing (2.3 h) and subsequently exhibit large absorption amplification (4.6 h). In contrast, achieving similar morphology and absorption variations requires much longer times (9 h and 18 h, respectively) in Houston. For fractal BC particles, there is negligible absorption variation, whereas compact BC particles exhibit noticeably enhanced MAC, with the maximum absorption enhancement factor of 2.4 for a coating fraction of unity. BC particles undergo rapid morphology modification in Beijing (2.3 h) and subsequently exhibit large absorption amplification (4.6 h). In contrast, achieving similar morphology and absorption variations requires much longer times (9 h and 18 h, respectively) in Houston.

**Absorption Enhancement.** The measured MAC in Beijing exhibits little change for a coating fraction of less than 0.5, but a large absorption enhancement occurs for a coating fraction of greater than 0.5 (Fig. 3). For the wavelengths of 405 nm and 532 nm, the largest absorption enhancement by factor of 2.4 is obtained for 150-nm and 220-nm particles. The measured MAC in Houston exhibits little change with a small coating fraction (<0.5). During the initial morphology change, a thin dielectric coating layer hinders the interaction of electromagnetic (EM) coupling between neighboring spherules, and the internal spherules are shielded by the outer ones, likely responsible for little absorption enhancement (8, 24).

For fully compact BC particles, efficient EM coupling between neighboring spherules contributes to an enhanced MAC, in addition to the lensing effect (15, 24). The Mie theory with the core–shell assumption for homogeneous spherical particles (25, 26) is used to calculate MAC. The measured and calculated absorption enhancements show comparable values for large coating fraction (>0.5) at both wavelengths (Fig. 3), but the Mie calculation yields absorption enhancement even for a coating fraction smaller than 0.5, because of the lensing effect (8).

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The basis of simulations from the previous global climate models (12). The DRF difference between fully aged and fresh BC particles increases by 0.45 W m\(^{-2}\) (Table S1), with a range of 0.21–0.80 W m\(^{-2}\) reflecting the uncertainty in the model simulations (Fig. 4).

**Atmospheric Implications.** Our results indicate that aging of BC particles under polluted urban environments exerts large impacts on air quality and climate (1, 2). For example, the enhanced optical properties of BC strongly influence visibility, air quality, and weather (3, 24, 30). Light absorption and scattering by BC lead to stabilization of the atmosphere, because of cooling at the surface and warming aloft (24). A stable atmospheric profile restricts vertical transport, which has a negative impact on air quality by accumulation of gaseous and particulate matter pollutants within the planetary boundary layer (PBL).

We illustrate distinct aging rates and resulting absorption enhancements of BC particles between Beijing and Houston, which are representative of those for urban cities in developing and developed countries (2). In both locations, BC particles exhibit noticeable morphology variations, but aging occurs much more efficiently in Beijing than in Houston. Our measured rapid aging and growth of BC particles in Beijing are consistent with the previous results by Guo et al., showing enormously efficient secondary photochemical growth of fine aerosols during the initial stage of haze development that is attributable to highly elevated levels of gaseous pollutants (18). The rapid morphology modification in Beijing (2.3 h) leads to large absorption amplification within a short time (4.6 h), in contrast to those for achieving similar morphology and absorption variations in Houston (9 h and 18 h, respectively). Hence, the rapid aging and largely enhanced absorption of BC particles (i.e., an absorption enhancement factor of 2.4 within a few hours) could contribute importantly to atmospheric stabilization and diminished diurnal PBL variation (2, 17, 18), exacerbating formation of severe haze events.

Currently, the results of absorption enhancement of BC particles during atmospheric aging from available experimental, theoretical, modeling, and field studies are conflicting, leading to large uncertainty in global radiative transfer calculations (12). Our measured absorption enhancement illustrates that the positive DRF of BC particles is highly dependent on the rate and the timescale of aging, which are currently unaccounted for in global climate models. Our results also provide a plausible reconciliation of the conflicting results of largely variable absorption enhancement and DRF of BC particles in the previous studies, i.e., an underestimated DRF in heavily polluted regions of East and South Asia predicted from a global climate model (29) but a low absorption enhancement measured in California (16). In addition, light absorption can be also enhanced by mixed BC and brown carbon particles (31).

Finally, our results suggest a distinction for BC particles between urban cities in developed and developing countries, i.e., a larger climatic impact in more polluted environments. It is commonly believed that improving air quality by reducing fine PM may counteract climate protection, because of the negative direct and indirect radiative forcings by nonabsorbing aerosols, in contrast to warming imposed by greenhouse gases (1). Our findings indicate that BC under polluted urban environments could contribute significantly to both pollution development and large positive radiative forcing, indicating that mitigation in BC emissions achieves a co-benefit in simultaneously controlling air pollution and protecting climate, especially for developing countries (1, 2, 32–34).

**Conclusions**

Using a novel environmental chamber approach, we have quantified the aging and variations in the morphology and optical properties of BC particles under ambient conditions in Beijing, China, and Houston, United States. Our results show that BC aging exhibits two distinct stages, i.e., initial transformation.
from a fractal to spherical morphology with little absorption variation and subsequent growth of fully compact particles with a large absorption enhancement. On the basis of our measurements, we have estimated the timescales of 2.3 h and 4.6 h, respectively, in Beijing to achieve complete morphology modification and an absorption amplification factor of 2.4 for BC particles, compared with 9 h and 18 h, respectively, in Houston. Our quantified BC morphology and absorption variations during aging are broadly applicable to diverse urban environments for improvement in radiative transfer calculations. Hence, our results have important implications for the assessments of the impacts of BC on air quality and climate.

Materials and Methods

The QUALITY chamber was divided into a lower flow chamber, where ambient air was pulled through continuously, and an upper reaction chamber, where the aging experiments were conducted (35). The two chambers were separated by a 5-μm-thick membrane, which allowed unimpeded penetration of ambient gases at a steady flow rate but filtered out ambient particles from the lower to upper chambers. The upper reaction chamber (1.2 m³) was made of PFA (perfluoroalkoxy) Teflon for efficient UV light transmission. Monodisperse fresh BC particles produced from incomplete combustion (10, 11) were introduced into the reaction chamber and exposed to sunlight. For example, the initial size and number concentration of BC particles introduced to the upper reaction chamber in Beijing were 195–224 nm and 800–4,200 particles cm⁻³, respectively, corresponding to a mass concentration in the range of 0.3–12 g m⁻³. A suite of high time resolution state-of-the-art aerosol instruments simultaneously measured a comprehensive set of BC properties throughout the BC aging process, including the particle diameter, mass, chemical composition, and optical coefficients (Fig. S1). The field measurements in Beijing were conducted on the campus of Peking University. The descriptions of the field sites and periods as well as ambient measurements in Beijing and Houston were provided previously (18, 19).

An integrated PM monitoring system, consisting of tandem differential mobility analyzer and aerosol particle mass analyzer (APM) was used to measure the aerosol mass-size relation, including the effective density, volatility, hygroscopicity, and DSF (18, 19). Aerosol optical properties were measured using three Photoacoustic Extinctiometers (PAX; DMT Inc.) in Beijing and a combined Cavity Ring Down Spectrometer (CRDS) and a nephelometer (3563; TSI, Inc.) in Houston (18, 19). The PAX used in situ photoacoustic technology to measure BC absorption. A laser beam directed through the aerosol stream was modulated at the resonant frequency of the acoustic chamber. Absorbing particles were heated up and quickly transferred heat to the surrounding air. The periodic heating produced pressure waves that were detected with a sensitive microphone. The system then determined the resonator quality factor and resonance frequency, which were needed to quantitatively determine aerosol light absorption. The laser wavelengths of the PAX are 405 nm, 532 nm, and 870 nm. The instruments were calculated with PSL (Polystyrene Latex Spheres) spheres and Aquadag soot particles, and zero check was performed automatically every 10 min. The CRDS measures aerosol extinction coefficients at 532 nm. During each experiment, an 11-ns 532-nm light pulse from a Q-switched laser was introduced into a stainless steel cell formed by two mirrors that had 99.998% reflectivity and an aerosol inlet in the center. Light exiting in the cavity was detected with a photomultiplier. The extinction coefficient was then calculated by nonlinear fitting of the averaged decay data.

The Mie theory with the core–shell assumption for homogeneous spherical particles was used to calculate MAC (25). The core–shell Mie model requires several input parameters, e.g., the size distribution of BC particles, the sizes of the inner BC core and outer shell, the refractive indexes of the BC core and coating materials (26). Because the core–shell Mie model assumes that all particles are compact spheres and both the BC core and outer shell are homogeneous, the core of aged BC particles is represented as the mass equivalent diameter (Dme) of fresh BC particle. The Dme of BC particles for the entire size range is calculated from

\[
D_{me} = \left( \frac{6k}{\rho_{BC}D_{fractal}^{3/2}} \right)^{1/6}
\]

where Dfractal is the fractal dimension for fresh BC particles, which is determined to be 2.25 in this study, and k is a constant. For aged BC particles, the size distribution of the core (Dcore) is equal to the size distribution of the mass...
equivalent diameter of fresh BC particle \( (D_{me,0}) \). Thus, with the assumption that the increases of mass equivalent diameter \( (\Delta D_{me}) \) are identical for BC particles within the entire size range, the mass equivalent diameter of aged BC particle is calculated by adding \( D_{me,0} \) and \( \Delta D_{me,0} \). The refractive index of fresh BC particles and the coating material used in this study are \( 1.91 + 0.71i \) and \( 1.55 + 0i \), respectively. For comparison, Bond et al. suggested a refractive index value of \( 1.95 + 0.79i \) for pure BC (12). In our study, the generated BC particles were measured to contain about 80% pure BC and 20% organic matter. Thus, the refractive index of fresh BC particles was estimated to be \( 1.91 + 0.71i \). The refractive index of coating material was measured in a parallel experiment without the injection of BC particles. In this experiment, new particles were produced by nucleation without seeded aerosols inside the chamber (36). By measuring the scattering and absorption coefficients, size distribution, and density of the particles formed, the refractive index was calculated to be \( 1.55 + 0i \) at the wavelength of 405 nm. Because the chemical composition of newly formed particles was similar to the coating material of the BC aging experiments, this refractive index value was considered to be representative of that of the coating material. The analysis of particle composition indicates the presence of dominant organic species as the coating materials in our experiments, formed from photochemical oxidation of VOCs (37–40). Because urban fine PM also contains a large portion of inorganic species (such as sulfate, nitrate, and ammonium), our measured BC aging rates and variations in the optical properties likely represent the lower limits under ambient conditions (17, 41). Also, note that the change in effective density implies change in refractive index. It has been suggested that the mixing rule (e.g., linear mixing and Lorentz–Lorenz mixing rule) may be appropriate to estimate the refractive index for an aerosol mixture (42).

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Supporting Information

Peng et al. 10.1073/pnas.1602310113

Fig. S1. Schematic depiction of the injection and measurement system of the QUALITY chamber experiments. A series of instruments were used to measure the BC particle properties, including a Scanning Mobility Particle Sizer to measure size distribution, a Differential Mobility Analyzer-APM (DMA-APM) system to measure the effective density, a high-resolution time-of-flight AMS (HR-ToF-AMS) to measure the chemical composition, a cloud condensation counter (CCN) to measure the hygroscopicity, and a photoacoustic extinctionmeter (PAX) to measure the optical properties. TDMA, tandem differential mobility analyzer; PTR-MS, proton transfer reaction–mass spectrometry.

Fig. S2. Correlation of the growth rate of the mass equivalent diameter ($\Delta D_{me}/\Delta t$) with $O_3$ (A), PM$_{2.5}$ concentration (B), photolysis rate coefficient for $O(1D)$ or $J_{O(1D)}$ (C), and temperature (D) in Beijing. Each point represents the average value for each experiment.
Table S1. Estimation of DRF and relative DRF between fully aged and fresh BC particles (ΔDRF)

<table>
<thead>
<tr>
<th>Model</th>
<th>Modeled MAC, m²·g⁻¹</th>
<th>Modeled fresh BC DRF, W·m⁻²</th>
<th>Scaled fully aged BC DRF, W·m⁻²</th>
<th>ΔDRF, W·m⁻²</th>
</tr>
</thead>
<tbody>
<tr>
<td>AeroCom models</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>GISS</td>
<td>8.4</td>
<td>0.22</td>
<td>0.53</td>
<td>0.31</td>
</tr>
<tr>
<td>LOA</td>
<td>8</td>
<td>0.32</td>
<td>0.77</td>
<td>0.45</td>
</tr>
<tr>
<td>LSCE</td>
<td>4.4</td>
<td>0.3</td>
<td>0.72</td>
<td>0.42</td>
</tr>
<tr>
<td>SPRINTARS</td>
<td>9.8</td>
<td>0.32</td>
<td>0.77</td>
<td>0.45</td>
</tr>
<tr>
<td>UIO-CTM</td>
<td>7.2</td>
<td>0.22</td>
<td>0.53</td>
<td>0.31</td>
</tr>
<tr>
<td>UMI</td>
<td>6.8</td>
<td>0.25</td>
<td>0.60</td>
<td>0.35</td>
</tr>
<tr>
<td>Other models</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CAM3 ECA</td>
<td>10.6</td>
<td>0.57</td>
<td>1.37</td>
<td>0.80</td>
</tr>
<tr>
<td>GISS-GCM II ext</td>
<td>7.8</td>
<td>0.51</td>
<td>1.22</td>
<td>0.71</td>
</tr>
<tr>
<td>GISS-MATRIX</td>
<td>8.2</td>
<td>0.15</td>
<td>0.36</td>
<td>0.21</td>
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<tr>
<td>UIO-CTM int</td>
<td>7.3</td>
<td>0.33</td>
<td>0.79</td>
<td>0.46</td>
</tr>
<tr>
<td>Average (min–max)</td>
<td></td>
<td>0.77 (0.36–1.37)</td>
<td>0.45 (0.21–0.80)</td>
<td></td>
</tr>
</tbody>
</table>

The model values are taken from Bond et al. (12): The BC emission and the MAC values correspond to those for the industrial era and externally mixed particles for all cases, respectively.