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The Discoloration of the Taj Mahal due to Particulate Carbon and Dust Deposition

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KEYWORDS: Brown Carbon (BrC), Black Carbon (BC), Dust, Surface Discoloration, Biomass Burning, Trash/Refuse Burning

Abstract

The white marble domes of the Taj Mahal are iconic images of India that attract millions of visitors every year. Over the past several decades the outer marble surfaces of the Taj Mahal have begun to discolor with time and must be painstakingly cleaned every several years. Although it has been generally believed that the discoloration is in some way linked with poor air quality in the Agra region, the specific components of air pollution responsible have yet to be identified. With this in mind, ambient particulate matter (PM) samples were collected over a one-year period and found to contain relatively high concentrations of light absorbing particles that could potentially discolor the Taj Mahal marble surfaces, that include black carbon (BC), light absorbing organic carbon (brown carbon, BrC), and dust. Analyses of particles deposited to marble surrogate surfaces at the Taj Mahal indicate that a large fraction of the outer Taj Mahal surfaces are covered with particles that contain both carbonaceous components and dust. We have developed a novel approach that estimates the impact of these deposited particles on the visible light surface reflectance, which is in turn used to estimate the perceived color by the human eye. Results indicate that deposited light absorbing dust and carbonaceous particles (both BC and BrC from the combustion of fossil fuels and biomass) are responsible for the surface discoloration of the Taj Mahal. Overall, the results suggest that the deposition of light absorbing particulate matter in regions of high aerosol loading are not only influencing cultural heritage but also the aesthetics of both natural and urban surfaces.

Introduction

On the timescale of several years the outer marble surfaces of the Taj Mahal become discolored and must be cleaned in a time consuming process (*1*). Figure 1 shows a cleaned section of a marble Mosque Dome at the Taj Mahal (where cleaning involves applying a layer of clay and removing the clay after it dries, followed by rinsing the surface with clean water) directly next to an area being prepared for cleaning. An obvious contrast is seen between the clean, white marble surface and the darker discolored surface of the Marble Dome. Many measures have been undertaken to avoid the impact of local air pollution, including restricting traffic within 1 km of the grounds and limiting the emissions of industrial pollution in the city of Agra, where the Taj Mahal is located. While detailed scientific studies have not been reported in the literature, past efforts focusing on the discoloration have hypothesized that local air quality is responsible and suggestions have included surface reactions with gas-phase SO_2, as well as aqueous phase chemistry linked with the deposition of fog droplets, and water condensation (*2*), as well as dust

FIGURE 1. A clean surface and an area being prepared for cleaning on a marble Mosque dome at the Taj Mahal

deposition *(1)*. Despite efforts to keep the outer surfaces of the Taj Mahal white, it continues to become discolored with time, and the reason for the discoloration is not currently understood. Recent work has reported poor air quality throughout the Indo-Gangetic plain *(3,4)*, including relatively high concentrations of particulate matter in Agra *(5-7)*. Particulate matter in the region includes the light absorbing components black carbon (BC), light absorbing organic carbon (a fraction of which can absorb light preferentially in the UV region and is often termed brown carbon, BrC), and dust (8). Both organic carbon and dust have the potential to preferentially absorb solar light in the blue region of the spectrum, which can give the atmosphere a brown hue and has thus been dubbed the Atmospheric Brown Cloud *(9)*. The presence of these light absorbing aerosols, and in particular those that can take on a dark hue against a light colored background, suggest that the deposition of ambient particulate matter may be playing a role in the discoloration of the outer white marble surfaces of the Taj Mahal.

Experimental Methods

Ambient Particulate Sampling and Analyses. In order to determine the influence of PM on the Taj Mahal, ambient aerosol sampling was conducted for a roughly one-year period beginning on Nov. 5, 2011 and continuing through June, 2012 just prior to the monsoon season. Filters were collected every 6^{th} day each month for both $PM_{2.5}$ (fine particulate matter having diameters less than 2.5 μm) and total suspended particulate matter (TSP), and analyzed for major anions, organic (OC) and elemental carbon (EC), and trace elements. The $PM_{2.5}$ cut-point was established using an upstream cyclone, while the TSP directly sampled ambient air. Portions of each filter were combined to make monthly composites that were extracted and analyzed for source specific trace organic compounds using GCMS. The trace organic concentrations were

used to estimate source contributions to particulate organic carbon using chemical mass balance (CMB) modeling *(10)*. Additional information on the sampling and chemical analyses is presented in the Supplementary Material section (sections S1 and S2).

Marble Deposition Target Sampling and Analyses. In addition to ambient samples, several pre-cleaned marble deposition targets (with dimensions 2 cm x 2 cm x 0.5 cm) were placed outdoors within roughly 300 m of the main Taj Mahal dome. Both the air sampling equipment and targets were located in a section of the Taj Mahal that was accessible only to staff of the Archaeological Survey of India (ASI), and had very little foot traffic. Pre-cleaned marble cuboids were fastened to Taj Mahal structures with double-sided tape at a variety of locations, and exposed from April to June 2012. Some of the marble samples were placed horizontally and others vertically. Prior to, and after exposure, the marble samples were placed in sealed, pre-cleaned petri dishes and stored in a freezer to avoid degradation of deposited particles.

Scanning Electron Microscopy (SEM) (LEO 1530, Carl Zeiss Microscopy) and Energy Dispersive X-ray (EDX) Spectroscopy (Oxford Instruments X_{max} detector) were carried out on two horizontally facing marble targets. Images were taken at many different magnifications to capture the particles having sizes ranging from 100 nm to 100 μm. The particle sizes and shapes were accessed through SEM images using image processing in a Matlab program. EDX analyses were carried out on the same marble targets on ~ 1000 particles. The information gained from the SEM/EDX analyses allowed for the estimation of the particle number and surface area concentration, and chemical composition as a function of area of the marble target. This information was then used, as described in the next sections, to estimate the change in color of

104 the marble surface. More information on the SEM/EDX analyses is given in the Supplementary
105 Material Sections S1 and S2.

106

107 **Linking Deposited Particles to Marble Surface Color**. In order to estimate the impact of
108 particles deposited to the marble substrate on the perceived color change of the surface, we
109 developed an approach that estimates the influence of deposited particles on wavelength-
110 dependent surface reflectance. The method builds on previous work that estimated the influence
111 of particles deposited to plant leafs on available photosynthetically active radiation *(11)*. First,
112 we use SEM/EDX analyses of particles deposited to the marble targets to estimate the optical
113 depth of deposited particles as a function of wavelength (τ_λ) as follows:

114 $$\tau_\lambda = \frac{\pi}{4}\sum_{i=1}^{n} Ac_i D_{p,i}^2 \left[Q_{s\lambda} + Q_{a\lambda}\right]_i \qquad (1)$$

115 Where Ac is the areal particle number concentration (number of particles deposited per area of
116 the marble surface) for each size bin, i, D_p is the particle diameter for deposited particles, and
117 $Q_{s\lambda}$ and $Q_{a\lambda}$ are the wavelength dependent Mie scattering and absorption efficiencies that are
118 determined based on particle size and composition.

119

120 After estimating the optical depth, the wavelength dependent single scattering albedo, ω_λ (ratio
121 of light scattering to extinction) is estimated as:

122 $$\omega_\lambda = \frac{\sum_{i=1}^{n} Ac_i D_{p,i}^2 Q_{s\lambda,i}}{\sum_{i=1}^{n} Ac_i D_{p,i}^2 \left[Q_{s\lambda} + Q_{a\lambda}\right]_i} \qquad (2)$$

The single scattering albedo is a key parameter that determines the relative amount of light absorption that occurs over the white marble surface. For white, scattering only particles the single scattering albedo is near 1.0 and the surface reflectance of a white surface will not change.

The change in the surface reflectance of the white marble surface is calculated using SBDART, a radiative transfer model *(12)* with input values including τ_λ and ω_λ estimated from equations 1, and 2 as well as the asymmetry parameter (relative amount of light scattering in the forward direction) as a function of wavelength using Mie theory *(13)*.

In order to determine the perceived color change of the white marble surface based on particle deposition, and the related change in spectral surface reflectance we used the model described by D'Andrade and Romney *(14)* to convert spectral reflectance to perceived color in the Munsell color system. The Munsell color system is based on three components that include the value (lightness/darkness), hue (color), and chroma (purity/saturation). The model used to estimate the perceived color of the marble surface with deposited particles uses the spectral reflectance from the radiative transfer model of the marble surface loaded with particles to estimate the Munsell color. The Munsell color estimate also takes into consideration the human eye response as a function of wavelength of incident light (the approach is described in more detail in the supplementary information, section S3).

Results and Discussion

Ambient Particulate Concentrations. Figure 2a shows the average mass concentrations of particulate organic carbon mass (OM), ions, dust and elemental carbon (EC) for both TSP and $PM_{2.5}$ over the sampling period. The mean daily concentrations (and standard deviations) of both TSP and $PM_{2.5}$ are 135 (55) and 60 (39) μgm^{-3}. The values are significantly higher than the annual World Health Organization (WHO) PM guidelines for PM_{10} and $PM_{2.5}$ of 20 μgm^{-3} and 10 μgm^{-3} highlighting the poor air quality in the region. The fraction of particulate matter greater than 2.5 μm is ~60%, and is due in large part to the coarse mode dust that increases from 15% of the $PM_{2.5}$ mass fraction to 30%

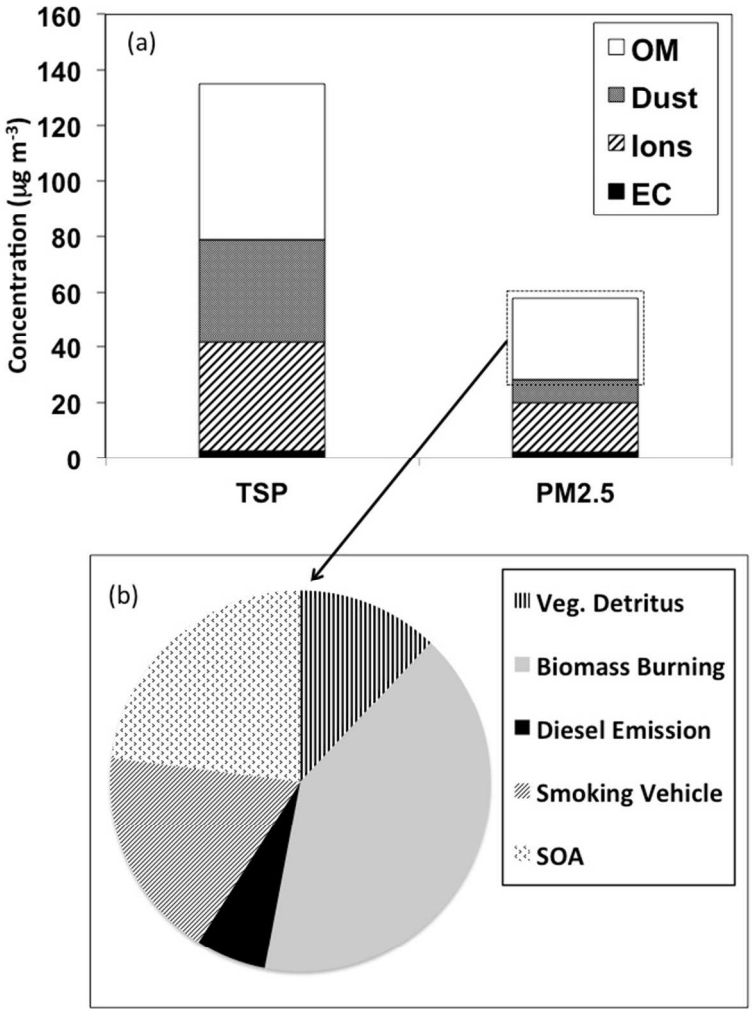

FIGURE 2. The general chemical composition of (a) Total Suspended Particulate matter (TSP) and fine particulate matter ($PM_{2.5}$), and (b) source apportionment of $PM_{2.5}$ organic mass (OM) based on filter sampling at the Taj

of the TSP mass. In addition to dust, other PM components that absorb light in the visible spectrum, and hence have the possibility to influence the color of the outer white marble surfaces, are elemental carbon (EC) that is responsible for 2% of the TSP mass, as well as OM that accounts for 39% of the TSP mass. Estimates of the sources of OM in the $PM_{2.5}$ mass fraction shown in Figure 2b indicate that biomass burning, a known source of BrC, is responsible for roughly half of the OM with significant contributions from vehicular emissions. It should be pointed out that biomass burning OM can be from a variety of activities including the combustion of wood and dung, crop residue, and the burning of trash and refuse that is ubiquitous in the region. The prevalence of light absorbing aerosols in Agra (i.e. elemental and organic carbon, and dust) suggests that PM deposition to the white marble surfaces may be responsible for the observed discoloration of the outer Taj Mahal structures including the famous Taj Mahal dome.

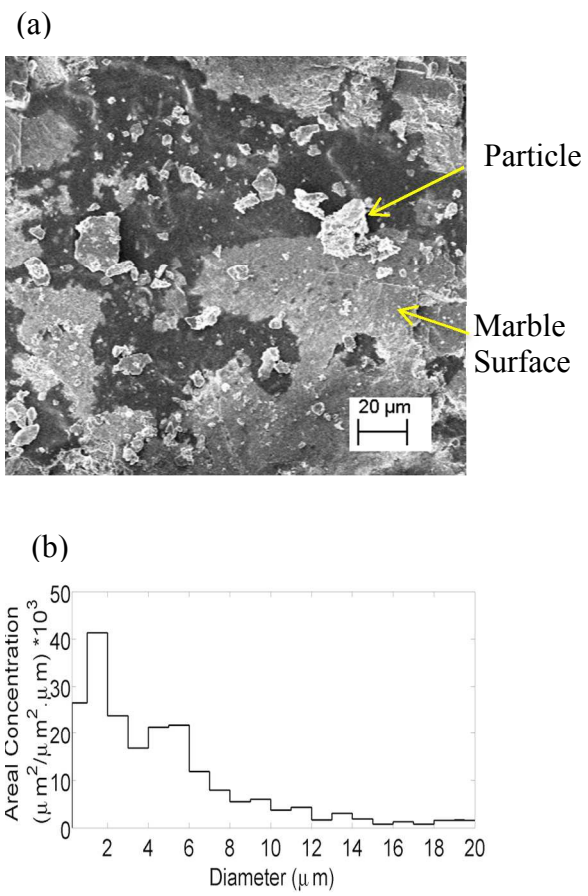

FIGURE 3. a) SEM image of marble target from Taj Mahal indicating deposited particles and b) surface area concentration of deposited particles on the marble target as a function of particle

Size and Composition of Particles Deposited to Marble Targets. Figure 3a shows a Scanning Electron Microscopy (SEM) image of a marble deposition target that was placed horizontally at the Taj Mahal, and was exposed for a roughly two month period during the pre-monsoon season of 2012. The surface area concentration (surface area of particles per unit marble surface area per micron) distribution of particles as a function of particle size deposited to the marble target (Figure 3b) shows peaks in particle size at roughly 1-2 μm, and an additional mode at 4-5 μm. The fraction of the surface covered by particles is estimated to be ~30%. Approximately 70% of the deposited particle surface area is for particles having diameters greater than 2 μm, indicating that a large fraction of the particle surface area concentration is due to the deposition of coarse particles. The dominance of coarse particles is due to both the relatively high concentration of dust particles measured in Agra, as well as the fact that the dry deposition velocity of coarse (~ 5 μm) particles is roughly 100 times greater than that of accumulation mode (~1.0 μm) aerosol particles *(15)*. It is likely that dry deposition is the dominant mode of particle transport to the Taj surface given the relatively low amount of precipitation in Agra during the Fall through Spring, when particle loadings are high and the summer monsoon rainfall is not occurring. It is also important to note that water insoluble particles (such as dust, BC, and a fraction of OM) are likely not easily removed from the Taj Mahal surface by precipitation wash-off once deposited. This is based on similar observations of the build-up of water insoluble particles on leaf surfaces observed in the Yangtze delta region of China, an area that also experiences high PM loadings (*11*).

The EDX analyses indicate that more than 70% of particles are primarily crustal in origin, with spectra dominated by crustal elements. The crustal particles were typically in the coarse (having

211 diameters greater than ~ 2-3 μm) size fraction. Particles having diameters less than 2 μm, which
212 account for roughly 30% of the deposited particle surface area, also contained significant
213 amounts of carbon likely from the sources of OM highlighted in CMB results in Figure 2b. More
214 detailed information on the EDX analyses, including example spectra of particle EDX analyses
215 are given in the supplementary section (S2).
216
217 **Deposited Particles and Perceived Color**. To estimate τ_λ we assume that particles having
218 diameters less than 3 μm are composed primarily of light absorbing organic carbon (BrC) with
219 wavelength dependent refractive indices reported by Liu et al. *(16)*. This assumption is based on
220 the fact that ambient filters indicated that roughly half of the $PM_{2.5}$ was carbonaceous in nature,
221 combined with the fact that we did not observe the presence of major ion related elements (i.e. S)
222 deposted to the marble targets, but did see a dominance of carbon particles in the less than 3 μm
223 particle sizes. We also assume that 10% of the particles less than 3 μm are black carbon (BC)
224 particles with a refractive index commonly used for soot particles *(13)*. It is likely that we
225 overestimate the influence light absorption by BrC and BC since we assume that all of the
226 particles less than 3 μm are carbonaceous and not elemental or ionic in nature. Aerosol optical
227 depth contributions at 400 nm for dust, BrC and BC are estimated to be 0.222, 0.144 and 0.016
228 respectively, highlighting the importance of light extinction by all three components. The single
229 scattering albedo at 400 nm and 700 nm is estimated to be 0.64 and 0.95, indicating that a
230 significant amount of light absorption occurs at near-ultraviolet wavelengths preferentially to
231 that at the longer 700 nm wavelength.
232

Figure 4a shows the surface reflectance of a pure marble surface as well as the estimated surface reflectance for several cases including the influence from each light absorbing particulate component separately (BC, BrC and dust), and the case when all components are combined. As seen in the plot, BC absorbs across all wavelengths evenly, with brown carbon showing preferential absorption at shorter wavelengths near 400 nm. Dust substantially reduces the surface reflectance at all wavelengths, and preferentially so at shorter wavelengths due to the presence of hematite, which absorbs at blue wavelengths. When combined, dust, BrC, and BC are estimated to substantially alter the surface reflectance with enhanced absorption (i.e. lower values of surface reflectance) at shorter wavelengths.

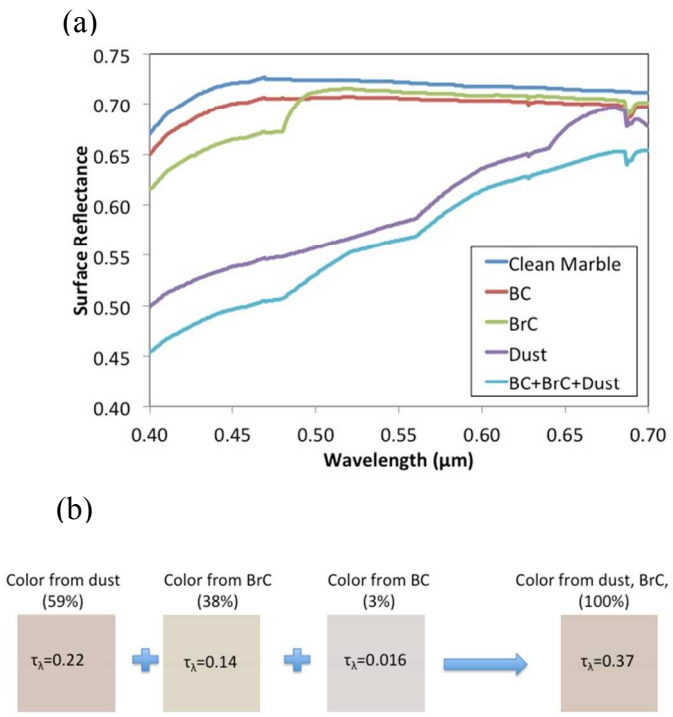

FIGURE 4. (a) Estimated marble target surface reflectance for a clean surface and surface area coverage of particles based on Fig. 3 for black carbon (BC), Brown Carbon (BrC), Dust and all particles (BC+BrC+Dust) (b) Change in color of white marble surface for dust, BrC, BC separately and combined. Values in parenthesis represent fraction of total surface area concentration contributed by each component with AOD values estimated by Eqn. 1 at 400 nm

Figure 4b shows the estimated change in color of the white surface for deposition of the light absorbing particles measured in Figure 3b over the two-month period the targets were exposed. Results indicate that separately each component contributes to the color change of the Taj Mahal white marble surfaces. For BC alone (which we estimate to account for 3% of the total particle surface area) the color change results in a greyish color given that the change in surface reflectance is proportionally similar at each wavelength. Both BrC (~30% of the total particle surface area) and dust influence color with preferential absorption in the UV resulting in yellowish-brown hues. When combined, the perceived color of the surface shifts towards darker shades of yellow-brown. It should be pointed out that our sample targets were mounted for a relatively short time (~2 months) compared to the typical time between cleanings of the outer Taj Mahal surfaces (several years), and therefore it may be expected that the perceived color of the marble target would be attenuated compared to that of the white surfaces of the Taj Mahal. Indeed the marble target surface did appear somewhat lighter in color as compared to the color estimates in Figure 4b, although qualitatively were similar. There are several uncertainties in estimating perceived color including the loading, particle size, and optical properties. Analyses (included in section S3) suggest that results are moderately sensitive to both particle loading and size. For example, assuming an uncertainty of 50% for aerosol loading only moderately influences the perceived color and does not change the conclusions that both dust and carbonaceous particles contribute to the perceived color change of the Taj Mahal. Overall, the results indicate that light absorbing particles play an important role in the discoloration of the Taj Mahal surface and that dust, as well as BC and BrC that are primarily from biomass combustion, trash/refuse burning, and mobile sources, all make significant contributions to the discoloration.

277 This work further suggests that the deposition of light absorbing particulate matter to both
278 natural and human-made surfaces results in a substantial discoloration in regions of high aerosol
279 loading. The discoloration impacts not only cultural artifacts but also the aesthetics of the
280 environment through the modification of surface albedo, and hence perceived color. The
281 measurement/modeling approach developed in this paper allows surface color changes to be
282 estimated based on the relative amounts of light absorbing particles deposited to surfaces, and
283 can be used to develop future control strategies to prevent the discoloration of the environment
284 by particle deposition, that will also improve air quality.

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289 Supporting information is associated with this paper and includes details related to filter and
290 marble surrogate surface sampling (S1), chemical analyses on both the filters and marble
291 surrogate surfaces (S2), as well as the approach to estimate perceived color based on surface
292 reflectance (S3). The information is available free of charge via the internet at
293 http://pubs.acs.org.

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