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Probable mixing state of aerosols in the Indo-Gangetic Basin, northern India

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[1] To investigate the probable mixing state of aerosols in the Indo-Gangetic Basin, six different mixing cases, *viz.* external mixing, internal mixing, and four combinations of core-shell type mixing (black carbon, BC over dust, water-soluble over dust, BC over water-soluble and water-soluble over BC) have been considered. Composite single scattering albedo (SSA) have been computed for six cases for post-monsoon, winter and pre-monsoon seasons and are compared with the Aerosol Robotic Network (AERONET) retrieved SSA values. The most probable mixing state in the post-monsoon season seems either to be external mixing or water-soluble coating over dust and in the winter season, the external mixing seems to be the probable mixing state. However, in the pre-monsoon season, BC coating over dust seems to be the most probable mixing state. This type of mixing leads to enhanced absorption and needs future attention to better understand the aerosol radiative effect in this region. **Citation:** Dey, S., S. N. Tripathi, and S. K. Mishra (2008), Probable mixing state of aerosols in the Indo-Gangetic Basin, northern India, *Geophys. Res. Lett.*, *35*, L03808, doi:10.1029/2007GL032622.

1. Introduction

[2] The role of aerosols in perturbing the climate through scattering and absorption (i.e. direct radiative effect) is well-known, yet the uncertainty in estimation of aerosol radiative forcing is large as compared to that of the greenhouse gases. One of the uncertain factors in the aerosol radiative effects is the mixing state of the aerosols [*Jacobson*, 2001; *Chandra et al.*, 2004]. Aerosols can either be externally mixed (different aerosol components existing separately) or internally mixed (each particle consists of different components). It has also been suggested that one component can form coating over another component to form core-shell type of mixing [*Jacobson*, 2001].

[3] The mixing state is more important in the regions where the natural aerosols mix with the anthropogenic components. Indo-Gangetic basin (IGB) in the northern India is such a region, where the natural mineral dusts are being transported from the western arid regions during the pre-monsoon season in every year [*Dey et al.*, 2004] and interact with the anthropogenic components as indicated by the presence of high concentration of Pb and Cd in the dust samples [*Chinnam et al.*, 2006]. In the other seasons, local soil-derived dusts contribute to the composite aerosol optical properties [*Dey and Tripathi*, 2007]. Recently, the aerosol direct radiative effect over the IGB was estimated over several key locations from ground-based measurements for the winter season, where the authors assume external mixing [*Dey and Tripathi*, 2007; *Ganguly et al.*, 2006; *Ramachandran et al.*, 2006]. However, the aerosol mixing state in the IGB is still unknown. In this paper, we attempt to infer the most probable mixing state for the aerosols in the IGB for the first time based on the direct measurements of aerosol chemical composition.

2. Approach

[4] Observations of aerosol physical, chemical and optical properties carried out in Kanpur (26.28°N, 80.2°E), a representative site in the IGB, are considered to simulate the optical properties [*Dey and Tripathi*, 2007]. We have considered absorbing black carbon (BC), scattering water-soluble components and dust in fine and coarse mode as the main aerosol species in this region following the measurements made by *Tare et al.* [2006]. Various mixing scenarios have been assumed and the resulting single scattering albedo (SSA) of composite aerosols was compared with the SSA retrieved by Aerosol Robotic Network (AERONET [*Holben et al.*, 1998]). All together, we have chosen six possible mixing cases as shown in Figure 1a; external (case 1), core-shell (four combinations, case 2–5) and internal mixing (case 6). Dust is not considered as shell in core-shell type mixing, as it is unlikely. In the core-shell type mixing, the composite aerosol optical property is computed assuming the external mixture between the core-shell combination and the remaining component. BC and water-soluble are considered as shell and dust as core in case 2 and 4 respectively. Case 3 denotes water-soluble as shell and BC as core and case 5 represents the vice versa.

[5] We have chosen October 2005 as representative of post-monsoon season, December 2005 as representative of winter season and March 2006 as representative of pre-monsoon season. Level 2.0 data of direct sun measurements by AERONET reveal that aerosol optical depth (AOD at 0.5 μm) are 0.716, 0.706 and 0.382 and Ångstrom exponent (α) are 1.174, 1.368 and 0.784 for October, December and March. From the optical properties, it can be concluded that the proportion of coarse mode particles is highest in the pre-monsoon season, followed by the post-monsoon and least in the winter season. The seasonal variability of AOD spectrum in Kanpur was already discussed elsewhere [*Singh et al.*, 2004]. During these months, mass concentrations of water-soluble and dust were derived from the chemical analysis [*Sharma*, 2006]. Aerosol samples were collected on Whatmann GF/A filter papers of size 8″ * 10″ using APM 450 Envirotech High-volume PM_{10} sampler, operated at a flow rate of 0.7–1.1 m^3 min^{-1} and the concentrations of

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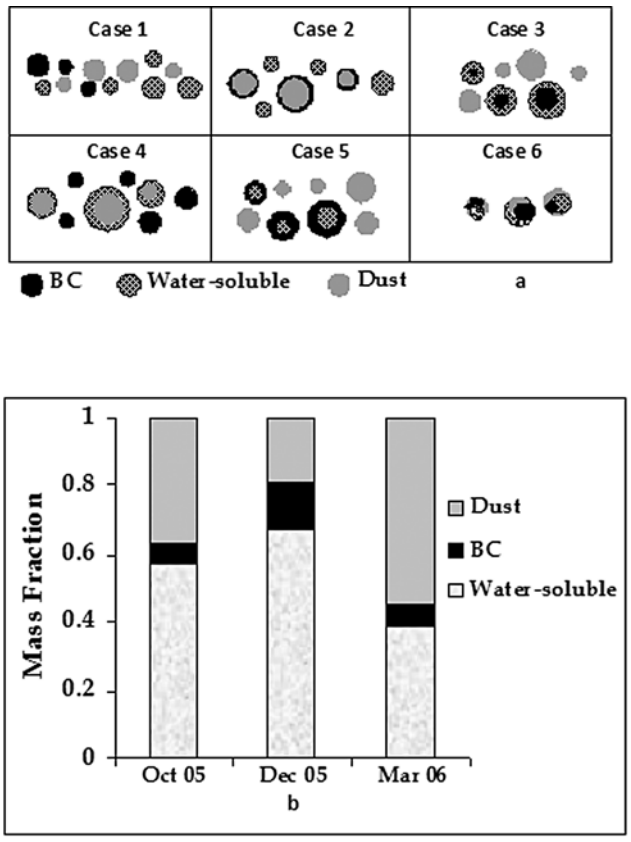

Figure 1. (a) Various mixing cases considered for this study. Case 1 represents external mixing, Case 2 represents dust and BC as core-shell combination externally mixed with water-soluble, Case 3 represents BC and water-soluble as core-shell combination externally mixed with dust, Case 4 represents dust and water-soluble as core-shell combination externally mixed with BC, Case 5 represents water-soluble and BC as core-shell combination externally mixed with dust, and Case 6 represents internal mixing. (b) Mass fraction of the three major components (BC, dust, and water-soluble) in the post-monsoon, winter, and pre-monsoon seasons over Kanpur.

water-soluble components are derived [*Tare et al.*, 2006]. Mass of the soil-derived dust was reconstructed using 'Al' to be 8% of the soil mass. BC concentration was measured by Aethalometer (Magee Scientific, USA). The mass concentration of dust is highest in March (22.68 μg m^{-3}), followed by October (12.3 μg m^{-3}) and December (10.46 μg m^{-3}), whereas, BC concentration is three times higher in December (7.78 μg m^{-3}) than in the other two months. The mass fractions are illustrated in Figure 1b, assuming that these three components constitute the composite aerosol in terms of the optical properties.

[6] For the winter season, the size distribution parameters of *Dey and Tripathi* [2007] are used for water-soluble and dust, whereas for other seasons and for BC in winter season, Optical Properties of Aerosols and Clouds (OPAC [*Hess et al.*, 1998]) database are used to convert the mass into number concentration. The size distribution parameters for water-soluble and dust in OPAC data base and given by *Dey and Tripathi* [2007] differ by ~15%. The volume size distribution of composite aerosol derived from the measured mass is also compared with that of AERONET. The coarse mode volume concentration in the model deviates from that of AERONET for particles greater than 5 μm. In this range the number concentrations of the particles are very less (in the order of 10^{-7}). In the fine mode, the measurements-derived volume concentration is lower than that of AERONET, which could be due to the unmeasured components, but the difference in the size distribution parameters is less than 10%. Sensitivity study shows that the SSA is more sensitive to the size distribution parameters, not the number concentration. The difference in the size distribution parameters between OPAC and *Dey and Tripathi* [2007] with AERONET, leads to an uncertainty of ~2% in the computed SSA.

[7] First, the extinction (b_{ext}) and scattering coefficients (b_{sca}) of each individual component are estimated at 0.45, 0.65, 0.9 and 1 μm wavelengths, as they are closest to the AERONET retrieval wavelengths (0.44, 0.67, 0.87 and 1.02 μm). The external SSA for composite aerosols (Case 1) is then estimated following *Dey and Tripathi* [2007].

[8] For core-shell type mixing, the code developed by Dr. W. Wiscombe, based on the work by *Toon and Ackerman* [1981], is used to compute the scattering and absorption by concentric spheres. The composite SSA is subsequently calculated for external mixture of core-shell combination and the remaining component [*Chandra et al.*, 2004]. The radius of the shell (R_s) can be calculated from the estimated mass of shell (M_s) in each size bin using:

$$R_s = \left(R_c^3 \frac{\rho_c}{\rho_s} + \frac{3M_s}{4\pi\rho_s n} \right)^{1/3}, \quad (1)$$

where, n is the number concentration of particles in a particular bin, R_c is the core radius for that size bin and ρ_s and ρ_c are the shell and core mass density. The M_s can be distributed either by equal distribution in each size bin of the core or by following the core number size distribution. As, the number concentration of the core species is very less in the coarse mode, the available mass to coat each single particle would be very large leading to very high shell-core ratio (see Figure S1a of the auxiliary material),[1] if first approach is taken. The shell-core ratio in the second approach is found to be relatively uniform throughout the size range (see Figure S1b). As the mass of water-soluble is much higher than that of BC, enough mass of BC is not available to coat all water-soluble particles in all size bins.

[9] Optical calculations for internal mixing (case 6) are performed using Mie code developed by *Lentz* [1976]. We have considered the volume-weighted average composite refractive index assuming the individual volume concentration of the components summing up to the total volume. The real and imaginary parts of the composite refractive index are calculated to be 1.448 and 0.0063 for October, 1.5 and 0.0074 for December and 1.565 and 0.015 for March with an uncertainty of ~3% due to assumption of individual refractive index. We have also examined the implications of non-sphericity of the dust particles to our calculations

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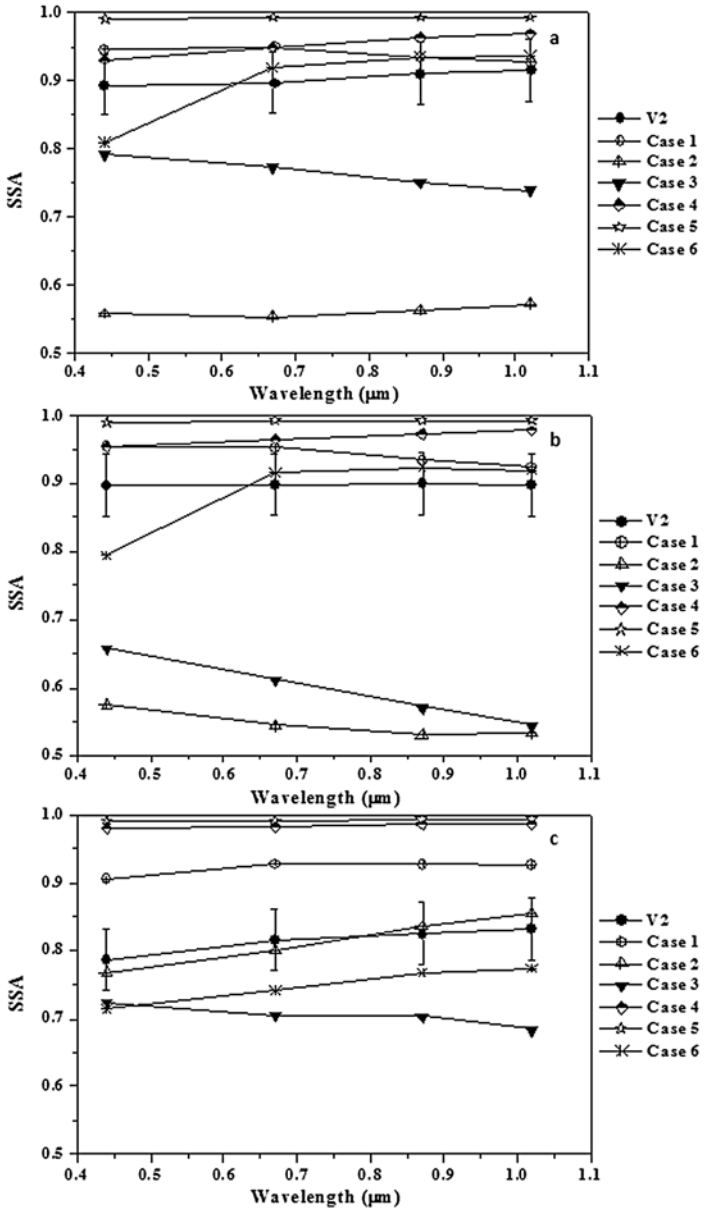

Figure 2. Composite SSA for 6 cases in (a) October 2005 (post-monsoon), (b) December 2005 (winter), and (c) March 2006 (pre-monsoon) along with AERONET-retrieved SSA using version 2 (V2) algorithm. The error bars at each wavelength represent the uncertainty range of AERONET retrievals for V2.

(see S2). The SSA spectral trend indicates that for aspect ratio >2.5, the χ^2 may show good matching, but it can not be specified from calculations; neither are there any measurements of non-sphericity in this region. Hence, we restrict ourselves in concluding only that the non-sphericity of dusts is important in the pre-monsoon season, but future in situ measurements are required to quantify it.

3. Results and Discussion

[10] To infer the most probable mixing state, composite SSA are computed for all six cases for the three months (Figure 2) along with the AERONET retrieved version 2 (V2) SSA values. AERONET V2 algorithm incorporates some changes in the existing algorithm [*Dubovik and King*, 2000] to make the retrieval better, particularly in presence of dusts. It accounts randomly oriented spheroids to account for dust extinction [*Dubovik et al.*, 2006]. V2 data shows lower SSA as compared to V1 data primarily due to more accurate surface reflectance characterization in V2, based on MODIS spectral measurements and ecosystem based BRDF models.

[11] Altitude profiles of BC were measured for these three seasons and that of total aerosol concentration for pre-monsoon and post-monsoon season over Kanpur using an aircraft up to 1.5 km [*Tripathi et al.*, 2007]. In absence of direct measurements of near-surface SSA, we have compared our results with the AERONET data, as the spectral variation of SSA along with the absolute values implies the true nature of aerosol radiative effects. The

best match is considered for lowest value of χ^2, where, $\chi^2 = \sqrt{\frac{1}{4}\sum_{i=1}^{4}\left(SSA_i^{AERONET} - SSA_i^{model}\right)^2}$, $SSA^{AERONET}$ and SSA^{model} are AERONET-retrieved and model-derived SSA and i indicates four wavelengths. Mainly we have considered the V2 AERONET product for comparison through χ^2 values unless otherwise mentioned. Cases 2 and 6 involve absorption by each particle and large water-soluble shell thickness in case 3 scatters more radiation towards the absorbing BC core, thus causing more radiation to interact with BC, and thus enhancing the total absorption. In case 5, BC coating on water-soluble particles only in fine size bins causes less absorption. We consider the size range from 0.01 to 10 μm, which encompass most of the aerosol mass that can affect the radiative properties [*Clarke et al.*, 2004].

[12] In the post-monsoon season, spectral SSA for cases 1 ($\chi^2 = 0.084$) and 4 ($\chi^2 = 0.098$) lie within the uncertainty range of AERONET-retrieved values. Case 6 shows close agreement at three wavelengths (0.67, 0.87 and 1.02 μm), but large difference (>10%) exists at the shorter wavelength. Case 2 is too low, case 5 is too high, and case 3 fails to capture the spectrally increasing trend. Coating of water-soluble over dust is common during the long-range transport [*Bauer and Koch*, 2005]. However, the factors controlling the uptake of water-soluble species over dust surfaces are complex and can not be commented with the present dataset.

[13] In the winter season, no case is found to be within the uncertainty range of AERONET V2 data for all the wavelengths. However, case 1 shows the best match ($\chi^2 = 0.09$), with SSA at 0.44 and 0.67 μm only ~1.4% higher than the uncertainty range of AERONET-SSA. Among the other cases, case 6 shows close match at three wavelengths, but high deviation (~17%) at 0.44 μm reduces the overall spectral match. In the wintertime, due to presence of foggy condition in this region, RH remains high, which increases the scattering by hygroscopic water-soluble particles, suppressing the absorption by each particle in relative scale [*Dey and Tripathi*, 2007]. Cases 4 and 5 show much higher scattering, whereas cases 2 and 3 show much higher absorption.

[14] In March 2006, BC mass (~2.6 μg m^{-3}) as well as BC mass fraction (~4.1 ± 0.2%) is lower as compared to those (BC ~ 7.8 μg m^{-3}, BC mass fraction ~8.5 ± 0.1%) in December 2005, but SSA in the March is lower and shows spectrally increasing trend. AERONET V2 data from 2001–2006 also reveals similar range of SSA in the pre-monsoon (0.86–0.92) and winter (0.87–0.89) seasons. The external mixing fails to explain this enhanced absorption, as SSA for case 1 is ~12% higher than AERONET V2 values. The internal mixing results in much higher absorption. Cases 4 and 5 display much higher scattering and insensitive spectral variation, whereas case 3 shows decreasing spectral trend. We have found that case 2 shows best match.

[15] In all the three seasons, only few cases show close agreement with AERONET-retrieved spectral columnar SSA. The discrepancy of the other cases could also be caused due to unknown aerosol vertical distribution above 1.5 km altitude. We have performed sensitivity test to check how much columnar aerosol SSA can be different from near-surface aerosol SSA due to aerosol vertical distribution. In post-monsoon and winter seasons, the aerosol vertical profiles in the IGB shows almost static trend and very low extinction values above 2 km [*Ganguly et al.*, 2006], which suggests that alteration in columnar SSA is unlikely. Only in the pre-monsoon season, dusts transported to the IGB above the boundary layer can alter the columnar SSA. We have also analyzed UV-aerosol index (indicating absorbing aerosols) using OMI/Aura satellite, over 0.25° × 0.25°grid surrounding the measurement site for March 2006 and found out that the values are much lower as compared to the values (>1.7) observed during the dust events in this region by *Dey et al.* [2004]. This indicates that dust is not present at much elevated height, as the UV-aerosol index is not sensitive to aerosols present at low altitude, particularly close to the boundary layer [*Mahowald and Dufresne*, 2004]. Keeping this fact in mind, we have considered dust layer between 2 to 3 km in our sensitivity study, while considering the vertical profiles of BC and water-soluble components constant above 1.5 km altitude. There are not enough BC particles available to coat dust particles aloft, but there is possibility that the elevated dust particles get coated by BC on the path of transportation. In that case, the presence of the dust layer would reduce the columnar SSA below 0.7. The internal mixing results in 7% lower SSA at 0.44 μm and 1–3% lower SSA at the other wavelengths. For cases 4 and 5, the spectral SSA is still higher. For case 1, the SSA of the dust layer aloft should be ~0.65 to obtain desire match. If the transported dust is that absorbing in nature, the external mixing could be a probable case, but *Moorthy et al.* [2007] have shown that SSA of dusts over the Great Indian Desert (a major dust source to the IGB) lies in the range 0.88–0.94. Hence, without further information on dust layer aloft, BC mixing with dust particles seems to be a probable mixing state in this period. In the ACE-Asia campaign, BC particles attached to the surface of dust particles at low altitude were observed [*Clarke et al.*, 2004]. The mixing of BC with dust would increase the absorption efficiency of dust particles in this region. *Moorthy et al.* [2007] have observed large dust absorption over Indian region and commented that this could be due to mixing of BC on dust particles, which is substantiated by our results. The core-shell mixing of dust and BC in the pre-monsoon season has important climatic implications, as the radiative impact due to dust would lead to heating rather than cooling. Our results further indicate the importance of investigation of BC-dust mixing in quantitative way in future.

4. Conclusions

[16] The various mixing scenarios of aerosols in the IGB have been investigated using the measured chemical composition at surface carried out in Kanpur in three distinct seasons and are compared with the AERONET-retrieved columnar SSA using the measured aerosol vertical profiles up to 1.5 km. With the limitations of aerosol vertical profiles, the major conclusions of our study are as follows:

[17] (1) The external mixing is the most probable mixing state in the winter, whereas the water-soluble coating over dust particles and external mixing emerge as the probable cases in the post-monsoon season. However, very close SSA values for the above cases imply that the external

mixing would be reasonable choice to compute aerosol radiative effects in these seasons.

[18] (2) The mixing state is, however, very different in the pre-monsoon season, when the BC coating over dust particles seems to be the most probable case. The other mixing cases result in higher scattering as compared to AERONET. The dust-BC mixing in the IGB would lead to enhanced absorption and further in situ observations, especially the distribution of dusts aloft are needed to address this issue more quantitatively.

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