SEASONAL SHIFT OF BLACK CARBON MIXING STATE AND ITS IMPACT ON SURFACE RADIATIVE FORCING

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ABSTRACT

We analyze the evidence for the change of mixing state of aerosols from winter to summer inferred from the clear-sky surface radiative fluxes measured over the Arabian Sea. Compared to the solar absorption calculated by assuming externally mixed aerosols, we find that the estimates are in agreement with the observations in January-March but become increasingly too low from spring to summer (April-August). The discrepancy can be corrected by assuming that black carbon is coated with sulfate oxidized from SO₂ or sea salt. The photochemical processing time of black carbon aerosols and SO2 increases as photochemical activity and the transport time for aerosols to reach the observation location increase substantially from winter to summer. Coating of sea salt on black carbon may also contribute significantly to solar absorption, increasing the efficacy of black carbon radiative forcing. While the assumption of external mixing is adequate for winter, it significantly underestimates the BC absorption in summer. Internal mixing assumption leads to significant overestimates in winter and summer. Seasonal change of mixing state such as the partial core-shell structure suggested in this study is needed in global and regional models for more reliable BC radiative forcing estimate.

KEY WORDS

Black carbon, radiative forcing, data modeling, climate change

1. Introduction

Aerosols are capable of changing incoming solar and outgoing infrared radiation (Charlson et al., 1992; Kaufman et al., 2003). The consequent change in radiation fluxes caused by aerosols is termed as radiative forcing (Intergovernmental Panel on Climate Change, 2007). Black carbon (BC) is the main radiation-absorbing component among aerosol species in the visible spectrum (Bond et al., 2006). Internally mixed BC has usually higher specific absorption (Fuller et al., 1999) than externally mixed BC because of increased absorption cross-sections associated with the larger sized internally mixed particles (Schuster et al., 2005). It has been reported that the black carbon aerosols can exist in one of several possible mixing states, externally mixed, internally mixed (Myhre et al., 1998; Jacobson, 2000) or a black-carbon core could be coated by a well mixed shell (Cheng et al., 2006; Spencer, et al., 2008; Péré et al., 2009). In radiative calculation, aerosols are usually assumed to be externally mixed, even though the radiative properties of aerosols are substantially different depending on the mixing state assumptions (Jacobson, 2001). Therefore, atmospheric simulations need to represent how BC aerosols are mixed with other aerosols (Adams and Seinfeld, 2002; Liu et al., 2005). Measurements of mixing state require single particle methods either in real time (Hughes et al., 2002) or using electron microscopy (Posfai et al., 1999; Johnson et al., 2005), which are sparse. Hence, in the absence of a proper data set on mixing state of aerosols, simulation from available data on aerosol optical properties, though highly challenging, is a feasible option for constraining the aerosol mixing state in the climate models.

Various studies have discussed the impacts of mixing state of aerosols on regional radiative balances (Rosen and Hansen, 1984; Riemer et al. 2003; Chandra et al., 2004 Schnaiter et al., 2005). Mixing state assumption has been reported to affect BC global direct forcing by a factor of 3 (+0.27 Wm⁻² for an external mixture, +0.54 Wm^{-2} for BC as a coated core, and +0.78 Wm^{-2} for BC as well mixed internally) (Jacobson, 2000). BC being solid, may not be well mixed internally within a particle, so the real forcing due to BC fall between an external mixture and that of a coated core (Jacobson, 2001). Based on the INDOEX (Indian Ocean Experiment) data at KCO (Kaashidhoo Climate Observatory), Republic of Maldives, it has been reported that during February and March (1998), measured and estimated (based on external mixing state assumption) surface radiative fluxes (diffuse and direct both) agree well within instrumental uncertainties (±3 W m⁻²), but during August (moist season) in the same year, surface diffuse radiative fluxes were overestimated by ± 23 Wm⁻² (Satheesh et al., 1999; Ramanathan et al., 2001).

Freshly emitted BC is mainly hydrophobic and externally mixed but with aging, it acquires hydrophilic coating (Martins et al., 1998; Conant et al., 2002; Bond et al., 2006) through interaction with atmospheric gases such as sulphuric acid and nitric acid and through oxidation (Zuberi et al., 2005). The aging process is dominated by the condensation of sulphuric acid with the time scale of about 8 hr near the source region in summer during the day (continental conditions, Central Europe and North America) while in winter ammonium nitrate becomes more important at the same time scale (Riemer et al., 2004). The impact of BC aging processes suggests that most of the aged carbonaceous aerosols in the troposphere are internally mixed with sulfate, nitrate and secondary organics (Riemer et al., 2004). Hence, there may be a seasonal shift of BC mixing state in the vicinity of source regions from winter to summer since photochemical processing is much faster in the summer. Such a signal can be inferred by comparing measured and model calculated (with different mixing state assumptions) surface diffuse radiative fluxes. We use this approach in this study to analyze the observations over the Arabian Sea from winter to summer. Back-trajectory analysis is applied to estimate the atmospheric processing of BC aerosols.

2. Measurements and Models

There were extensive aerosol measurements over the Arabian Sea region and along its coasts (4°N-20°N to 50°E-78°E) for eight years from 1995 to 2002 (Satheesh et al., 2004). Here, we used the observations at a site (15.4°N, 73.8°E) located within this region for the year 1999, when all necessary data for this study are available, to understand and characterize the seasonal (January-August) variations in the physical, chemical, and radiative properties of aerosols over the Arabian Sea. Measurements of aerosol optical depth (AOD) in five spectral bands from 400 to 1050 nm were made using a Sun-photometer and aerosol mass concentrations in ten size bins ranging from 0.05 to 25 µm diameters were made using a sensitive quartz crystal cascade impactor system. The contribution of organic aerosols to the AOD is not significant compared to inorganics and they have been considered together with ash. The Hygroscopicity Tandem Differential Mobility Analyzer (HTDMA) measurements of hygroscopic properties of atmospheric particles at initial dry sizes (Dp) of 50, 150, and 250 nm and at relative humidities (RH) of 30, 55, 75, and 90% were used to estimate the size distribution of the aerosols at ambient conditions by multiplying with the growth factor. Global and diffuse radiative fluxes were measured using broadband radiometers with narrowband filters. Measurements using the Particle Soot Absorption Photometer (PSAP) and Nephelometer were used to compute the single-scattering albedo (SSA) and characterize absorptive aerosols.

While BC aerosols are initially hydrophobic, they become hydrophilic with chemical aging (Kojima et al., 2004; Hinz et al., 2005; Stier et al., 2006; Ervens et al., 2007). Significant fractions of black carbon by mass may not be externally mixed with other compounds but are coated with water-soluble compounds such as sulfate and organic carbon [Posfai et al., 1999; Novakov et al., 2000; Hitzenberger and Tohno, 2001]. In this study, we assume a fraction of BC is coated with either sulfate or sea salt, while the rest is externally mixed. In order to estimate the asymmetry factor and AOD on the basis of available aerosol measurements, we used the code developed by Dr. Warren Wiscombe (NASA/GSFC) based on the work by Dave et al., (1968) and Toon and Ackerman (1981) to treat light scattering and absorption by a spherical shell; the shell and core are assumed to have different optical properties. We have the distributions of different aerosols in different size bins from .005-50 µm. When we assume a certain mass fraction of BC aerosols is forming coreshell structure, we mix the same mass fraction of aerosols in each size bin forming core-shell with the sulfate or sea salt or sulfate aerosols. We then apply the estimated asymmetry factor and AOD and measured SSA values in the DISORT (Discrete Ordinates Radiative Transfer Program for a Multi-Layered Plane-Parallel Medium) (Stamnes et al., 1989) to estimate radiative fluxes. We adjust the coated BC aerosol mass fraction in order to reproduce the observed (diffuse) radiation fluxes. Our calculations show that coating with sulfate or sea salt gives similar results when different physical and optical properties of sulfate and sea salt aerosols are taken into account in the calculation of the mass fraction of coreshell structure; therefore we show only the results with sulfate coating. The Weather Research and Forecasting (WRF) model (v3.0, Skamarock et al., 2005) was used to assimilate the meteorological fields on the basis of the NCEP reanalysis products. The model domain centers at 15.4°N, 73.8°E with a size of 10°x25°. The model horizontal resolution is 10 km with 23 layers in the troposphere. WRF simulated boundary layer heights were used to estimate monthly AOD values in the region assuming aerosols to be well mixed within the boundary layer. Kinematic backtrajectory calculations (Arimoto et al., 2008) were carried out using WRF meteorological fields.

3. Results and Discussion

We calculate surface diffuse solar fluxes assuming that BC aerosols are only externally mixed and find that calculated values are generally higher than the observations. indicating insufficient atmospheric absorption in the model. Here we use refractive indices of different aerosols from Bond and Bergstrom (2006) and the density of BC aerosols (1.8gm/cm³) (Schwarz et al. 2006). The model bias is small in winter but increases rapidly to summer. We define the difference of simulated from observed diffuse flux as excess flux and show the increase of the excess flux from winter to summer in Figure 1. The average excess radiative flux as a function of month increases from 3-4 Wm⁻² in January-March, monotonically to 32 Wm⁻² in the month of August. On a global scale, it has been suggested that if the BC abundance is increased 2-3 times the measured and estimated global fluxes (assuming externally mixed aerosols) would agree well (Sato et al., 2003). In this study, if we increase BC aerosols mass by a factor of 2,

the measured and estimated solar diffuse surface radiative fluxes agree well within the measurement uncertainties. However, we note that the excess flux increases towards summer, the observed abundance of BC in fact decreases (Figure 1) from 800 ng m⁻³ in (January-March) to 100 ng m⁻³ (August). Similar results of decreasing BC mass have been reported by other studies from winter to summer (Babu et al., 2004). Hence, the possibility of increasing BC abundance to account excess fluxes is ruled out.

The monthly trend of observed SSA is shown in Figure 2, and is compared with the model results assuming external mixing, internal mixing, and core-shell structure. We note that the single scattering albedo is lowest in case of internal mixing case and is highest in case external mixing case, i.e., absorption is highest when BC aerosols are internally mixed. The low SSA values (0.86-0.94) observed over the Arabian Sea region indicate the presence of absorbing aerosols. The observed SSA also shows a decreasing trend towards August, indicating increased absorption during summertime (Zhu et al., 2007), while the abundance of EC decreases (Figure 1).



Figure 1. Monthly (January-August) variations in aethalometer-observed BC loading (ng/m³) and excess surface diffuse radiative fluxes. Excess flux here is defined as the difference between observed and calculated flux assuming that aerosols are externally mixed.



Figure 2. Monthly (January-August) variations in observed and modeled aerosol single scattering albedo (SSA) values assuming aerosols to be externally mixed, internally mixed, and forming core-shell structure. The blue line shows simulated values assuming that a fraction

of the BC aerosols is coated by Sulfate (5% in March, 12% in April, 15% in May, 21% in June, 24% in July, and 32% in August).

In the core-shell coating BC aerosols with sulfate or sea salt aerosols, we assume the same mass fraction of BC is coated by other aerosol species such as sulfate or sea salt in all observed size bins and calculate this fraction in order to match the observed SSA values and diffuse radiation at the surface. In the model calculation, the highest SSA value of 0.94 corresponds to external mixing. For the observed SSA values < 0.94, the calculation indicates that the coated BC mass fraction (of sulfate) increases, 5% in March, 12% in April, 15% in May, 21% in June, 24% in July, and 32% in August. As the season progresses, a larger fraction of BC appears to be hydrophilic at the observation location. Consequently, simulated SSA values are in agreement with observations (Fig. 2) showing the significant decrease from winter to summer. We also compare the simulated absorption coefficient with calculated core-shell mass fraction with the observed value and find good agreement.



Figure 3. Speciated aerosol contributions to aerosol optical depth at 550 nm when BC aerosols are assumed to be (1) externally mixed, (2) coated by sulfate, and (3) coated by seasalt. 100% coating is assumed to demonstrate the effects for the month of August.

We also looked at the sensitivity of aerosol optical depth on the mixing state of aerosols. Figure 3 shows the impact of mixing state on total aerosol optical depth at 550 nm for the month of August. When forming the coreshell structure, we assume that BC is fully coated by 100% of either sulfate or sea salt. The aerosol optical depth of BC aerosols coated with sea salt or sulfate is higher when they are forming core-shell structure than when they are externally mixed while the relative contributions from other aerosol components are lower. Changes in the aerosol optical depth in conjunction with the changes in SSA of aerosols show the impact of mixing state on radiative impact of aerosols.

Figure 4 shows the comparison of observed and simulated surface diffuse radiation for August. Using the external mixing assumption, the model would overestimate the surface diffusive by 32 W m⁻², implying that absorption by BC is underestimated. When 30% of BC is assumed to be coated by sulfate, the simulated flux is in good agreement with the measured values. The impact on radiative forcing by the change of mixing state is as large as 30% higher than the absorption by externally

mixed BC. The enhanced atmospheric absorption cools the surface significantly.

We investigate the sensitivity of estimated BC impacts on surface radiative flux to its mixing state by computing the difference of the observed and simulated surface diffuse solar radiative fluxes with different BC mixing state from the simulated flux without BC aerosols (Figure 5). In the month of March there is a dip in the radiative fluxes as shown in Fig. 5, which is due to the reduction in BC concentration and increase in solar flux. If external mixing is assumed, the effect is BC absorption varies from 5.2 to 20 W m⁻², generally increasing from winter to summer. When using the internal mixing assumption, the effect of BC absorption is higher by a factor of 2 in winter and it increases to a factor of 4 in summer (85 W m⁻² in August). The observations indicate closer agreement to external mixing in winter and to internal mixing in summer. We explain this result by suggesting that the core-shell coating of BC aerosols increases from winter to summer, leading to significantly more absorption than external mixing but less than internal mixing in summer (50 W m⁻² in August).



Figure 4. Observed and simulated surface diffuse radiative fluxes assuming externally mixed aerosols (red circles) or a fraction of BC aerosols (32%) coated by sulfate (blue circles) over the Arabian Sea for August.

After emission, BC is subject to atmospheric processes, which include oxidation, condensation and coagulation. These processes often referred as the aging processes act to change the hygroscopicity of the BC aerosol. The seasonal shift of mixing state estimated in this study could reflect the aging process of BC aerosols. The mixing state of BC aerosols is a function of aging because freshly emitted BC aerosols are hydrophobic and with aging BC aerosols are coated with hydrophilic aerosols, (Moteki, N., et al., 2007; Shiraiwa, M., et al., 2007; Oshima, N., et al., 2009). From spring to summer, photochemistry becomes increasingly active (Wang et al., 2003). More active photochemical oxidation in summer (due to large seasonal variation in daily average temperature and more exposure to sun-light during summer) accelerates the chemical aging process and the BC aerosols tend to be more hydrophilic (e.g., Chen et al., 2009). WRF meteorological simulations show that transport to the observation locations is mostly over land during early spring. The transport pathways in the summer are over the ocean and there is a clear transition in the transport pathways from spring to summer. The simulated transport pathways indicate much more exposure to sea salt aerosols in summer than winter. Furthermore, more active photochemical processing in summer results in faster oxidation of SO₂ and production of sulfate. Active photochemical oxidation also produces semi-volatile organics that can condense to existing particles (Robertson and Clarke, 2000). The coagulation and condensation processes also tend to change hydrophobic BC aerosols to hydrophilic aerosols at a rate faster than oxidative processes (Pierce et al., 2007). One of the uncertainties in this study is that the relative importance of sea salt, sulfate, and organics in BC coating cannot be determined due to a lack of the observational constraints.



Figure 5. Difference of observed and simulated surface solar diffuse radiative flux (including all aerosols) corresponding to external, internal, and core-shell mixing state and simulated flux from the simulation without BC aerosols

4. Conclusion

We analyze the measurements of aerosol size, composition, and SSA and clear-sky surface radiative fluxes over the Arabian Sea. BC is found to be the major absorber. If external mixing is assumed, model estimated surface diffuse radiative flux becomes increasingly lower than observed from winter to summer. We calculate the fractions of BC coated by sulfate or sea salt in order to explain the observed surface radiative flux. The results indicate that a much larger fraction of BC is coated in summer than spring, although the chemical nature of the coating cannot be determined from the measurements. The increased photochemical processing from winter to spring could expedite the aging process of BC aerosols and make them more hydrophilic. The greater exposure to sea salt in summer could be another reason. The indirect evidence provided here suggests that atmospheric radiative absorption is increased by as large as 30% due to the change of mixing state compared to the absorption by externally mixed BC. While the assumption of external mixing is adequate for winter, it significantly underestimates the BC absorption in summer. Internal mixing assumption leads to significant overestimates in winter and summer. Seasonal change of mixing state such as the partial core-shell structure suggested in this study is needed in global and regional models for more reliable BC radiative forcing estimate.

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