Atmospheric chemistry and climate

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Atmospheric chemistry is a branch of atmospheric science where major focus is the composition of the Earth's atmosphere. Knowledge of atmospheric composition is essential due to its interaction with (solar and terrestrial) radiation and interactions of atmospheric species (gaseous and particulate matter) with living organisms. Since atmospheric chemistry covers a vast range of topics, in this article the focus is on the chemistry of atmospheric aerosols with special emphasis on the Indian region. I present a review of the current state of knowledge of aerosol chemistry in India and propose future directions.

Keywords: Aerosols, atmosphere, chemistry, climate.

Introduction

ATMOSPHERIC chemistry is a branch of atmospheric science where major focus is the composition of the Earth's atmosphere and that of other planets; it is a multidisciplinary field of research[1–4]. Studies on the composition and chemistry of the atmosphere are important due to several reasons. Knowledge of atmospheric composition is essential to study interactions of the atmosphere with solar and terrestrial radiation, atmospheric correction in satellite remote sensing applications, interactions of atmospheric species (gaseous and particulate matter) with living organisms and so on[4,5].

Initial reports on the atmospheric composition began to appear in the 18th century. In the late 19th and early 20th centuries, trace species (constituents with very small concentrations) gained importance. Discovery of ozone in 1840 is one of the important milestones in the history of atmospheric chemistry. In India, even though studies of trace species began several decades ago, composition of particulate matter remained unknown until late 1990s. Atmosphere consists of gases and minute particles of solid and liquid matter (particulate matter known as atmospheric aerosols) in concentrations that can affect environment and health. While trace gases are relatively better understood, in this article the focus is on aerosol (particulate) chemistry.

Atmospheric aerosols are particles of solid or liquid phase dispersed in the atmosphere[4,6–11]. Aerosols are produced either by the mechanical disintegration processes occurring over land (e.g. lifting up of dust) and ocean

(e.g. sea-spray), or by chemical reactions occurring in the atmosphere (e.g. conversion of sulphur dioxide to sulphuric acid droplets)[6–8]. After production at one location, aerosols are often carried to locations far away from their sources. Most of the aerosol sources are located near the Earth's surface and hence their concentration (mass per unit volume) is larger near the surface. Occasionally there may be layers aloft depending upon the atmospheric conditions and transport phenomena. Aerosols can vary in size from 10^{-3} to 10^{2} μm depending upon the source and production mechanism. Small aerosols (<1 μm in size) are produced mainly by the nucleation of volatile gases, a process known as gas-to-particle conversion, in the atmosphere. Small aerosols often grow in size due to coagulation and by condensation of water vapour. Large aerosols (>1 μm in size) are produced directly by mechanical processes (e.g. action of winds). Aerosols of different size ranges are important for different atmospheric processes. While sub-micron aerosols (< 1 μm) are important in atmospheric optics, super-micron particles have important role as cloud condensation nuclei.

Atmospheric aerosols are of natural and anthropogenic origin. On a global scale, the natural sources of aerosols are three to four times larger than the anthropogenic ones, but regionally anthropogenic emissions can be significant[4,9]. Aerosols can have significant influence on the Earth's climate, although making up only one part in a billion of the mass of the atmosphere. Estimation of aerosol effect on radiation is more uncertain than that due to well-mixed greenhouse gases, because of their short lifetimes, highly inhomogeneous spatial distribution and their complex nature of interaction with radiation[12]. Although the aerosols have potential importance in climate studies, they are poorly characterized in climate models because of the lack of comprehensive database.

Systematic studies on atmospheric aerosols were virtually non-existent in India till 1980 (except a few isolated studies). During the Indian Middle Atmosphere Programme (IMAP), a series of experiments were conducted using ground-based, balloon-borne rockets and satellite techniques, and a project was initiated to monitor the aerosol characteristics over the Indian region by setting up observatories at a few selected sites. IMAP has sown the seeds for conceptual networks for aerosols, radiation and trace gases, and some of these have evolved subsequently to grow into national endeavours under well-focused programmes. A network which evolved under ISRO–GBP over nearly two decades is the Aerosol

Radiative Forcing over India Network (ARFINET), and facilitates the long-term observations of aerosols over distinct geographical environments and to assess their impacts on regional climate forcing[13,14]. Locations of ARFINET observatories are shown in Figure 1. Aerosol trends indicate conflicting trends at different regions of India, thereby reflecting the complex factors which controls various sources. While an increasing trend in aerosols has been observed in many cities, some have shown a decreasing trend during the last few years. Studies by the Central Pollution Control Board (CPCB), which runs a network of 342 observing stations across India, have revealed that the Respirable Suspended Particulate Matter (RSPM) at several stations far exceeds the National Ambient Air Quality Standards (NAAQS)[15]. A decreasing trend in sulphur dioxide levels has been observed in many cities and this could be due to various measures taken, such as reduction of sulphur in diesel and use of LPG instead of coal as a domestic fuel[15]. On the other hand, a decreasing trend has been observed in nitrogen dioxide levels probably due to various measures taken for vehicular pollution control, such as stricter vehicular emission norms. Vehicles are one of the major sources of nitrogen dioxide in the country. However, Delhi observed an increasing trend in the past few years, especially after the introduction of CNG[15].

Based on the measurements made during the past 20 years, it is obvious that there has been a steady increase in the aerosol loading in the Indian region[15–18]. The concentration of aerosols in the Indian region has reached high values and may have adverse impacts on our regional climate, agricultural production and health. Some researchers have argued that aerosols cause air quality degradation in the Asian region during winter[19–21]. Others speculate that the presence of aerosols may have an impact on ozone production in this region.

The large increase in aerosols can have a direct impact on agriculture as well. Chameides *et al.*[22] have examined the impact of aerosols on rice and wheat production in China. They have shown that the decrease in solar radiation at the surface (on account of aerosols) has a direct impact on rice and wheat production. They have used experimental data and models to show that a 30% reduction in solar radiation has decreased the yield in crops by as much as 30% in China. Considering the large values of aerosol concentration over India, a similar reduction of crop yield can occur in Punjab and Haryana on account of aerosols.

Chemical composition of aerosols

Aerosols produced from different natural and anthropogenic sources are mixed together in the atmosphere and hence each aerosol particle is a composite of different chemical constituents[7,8]. The chemical composition of aerosols determines their complex (containing real and imaginary parts) refractive index. Particle refractive index is an important parameter while determining its radiative effects. The real part determines its scattering properties and imaginary part, the absorption characteristics. The chemical composition and hence refractive index depends on the source of the particles. The real part of the particle refractive index usually lies in the range 1.3–1.6 and imaginary part varies over several orders of magnitude from about 5×10^{-9} to 5×10^{-1}. Particles originating from combustion (burning) processes usually have high absorption properties and hence high imaginary part of refractive index.

Aerosols, in general, consist of sulphates, nitrates, seasalt, mineral dust, carbonaceous components such as black carbon (BC; often called soot) and organic carbon (OC). Table 1 lists real and imaginary parts of the refractive indices of various species.
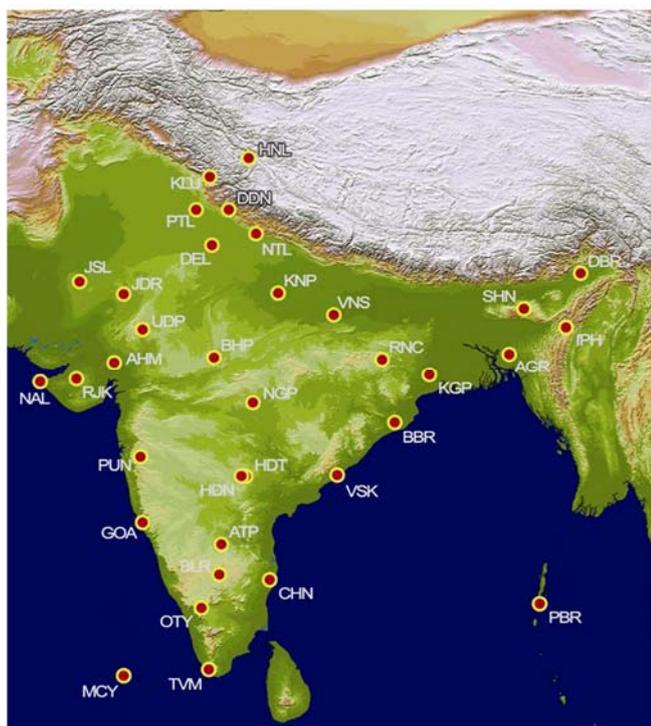

Figure 1. Locations of ARFINET sites marked on a digital elevation map of India.

Table 1. Real and imaginary parts of refractive indices of various aerosol species

Aerosol component	Real part	Imaginary part
Sulphates, nitrates	1.438E	-2.649×10^{-3}
Black carbon	1.750E	-4.5×10^{-1}
Dust	1.530E	-7.8×10^{-3}
Sea-salt (fine mode)	1.375E	-4.49×10^{-9}
Sea-salt (coarse mode)	1.374E	-4.465×10^{-9}

Sea-salt aerosols

Sea-salt particles are produced over the sea mainly by the processes associated with the bursting of bubbles[23-25]. When there are very strong winds with speeds $U >$ 10 m s^{-1} direct sea-spray production takes place by the breaking of wave crests. At moderate wind speeds of ~3–5 m s^{-1}, white capping occurs as the ocean surface waves overturn, thus generating bubbles. Liquid droplets injected into the marine atmosphere as a consequence of bubble bursting are called *jet droplets*. During bursting of bubbles the break-up of the bubble film produces a shower of small particles called *film droplets*.

After production the sea-water droplets evaporate in order to maintain equilibrium with the ambient relative humidity (RH). Depending on the RH, the particle can exist either as a solution droplet or crystalline matter. It has been suggested that sea-salt production rate not only depends on the sea surface wind speed, but also on sea surface temperature[26]. Due to hygroscopic in nature sea-salt particles are very efficient cloud condensation nuclei. Feingold *et al.*[27] showed that large sea-salt particles are able to significantly modify stratocumulus drizzle production and cloud albedo. Thus, sea-salt aerosols are major players in modifying the planetary albedo and hence play an important role in the Earth's radiation budget. The production of sea-salt aerosols, their transport, size distribution and wind-speed dependence have been extensively reported[23,25,28-32].

Sulphate and nitrate aerosols

Sulphate and nitrate aerosols are produced mainly due to anthropogenic activities[7,8]. Sulphate is formed by aqueous phase reactions within cloud droplets, oxidation of SO_2 via gaseous phase reactions with OH, and by condensational growth onto pre-existing particles[33,34]. The SO_2 emissions to the atmosphere are mostly related to fossil fuel (72%) burning and to a smaller extent to biomass burning (2%). The major sulphur compounds in the atmosphere are sulphur dioxide, hydrogen sulphide, carbon disulphide, carbonyl sulphide and dimethyl sulphide. Sulphate aerosols are also produced naturally over the oceans by the emissions from oceanic phytoplankton[35,36]. The dimethyl sulphide (DMS) emitted by oceanic phytoplankton (biogenic origin) is converted to sulphate aerosols over oceans. DMS-derived aerosols constitute 19% to the total sulphate aerosols in the atmosphere. Volcanic eruptions also emit sulphate aerosols (~7%) into the atmosphere. Their presence in the atmosphere scatters the solar radiation and increases the planetary albedo. These aerosols are hygroscopic in nature, and hence act as cloud condensation nuclei. It is believed that on a global scale, sulphate aerosols cool the planet and partly offset the heating due to greenhouse gases.

Atmospheric nitrate generally arises from the oxidation of nitrogen dioxide to nitric acid, which forms particles as a result of its reaction with ammonia or with sodium chloride[37]. The most common pure nitrate particulate matter is ammonium nitrate (NH_4NO_3). The precursor gases of particulate nitrate include nitrogen oxides, volatile nitrogen-bearing acids and gaseous nitrates[38].

Mineral dust aerosols

Mineral dust aerosols are produced over arid and semi-arid (dry) regions by the action of surface winds[39]. The chemical composition of mineral dust aerosols varies widely depending on the soil characteristics of the region of their production (origin). It has been shown that in the absence of convection, surface temperatures can be reduced by ~1 K beneath the dust layers[40]. The long-range transport of mineral dust by the combined action of convection currents and general circulation systems make these particles significant constituents even at locations far from their sources. Several studies have observed Saharan dust even at remote locations of the Atlantic Ocean (thousands of kilometres away from the source). Dust from the Sahara Desert is carried over the Atlantic Ocean by winds. Similarly, large-scale transport of dust occurs from Africa to the south Indian Ocean, from West Asia (Arabian region, Afghanistan, etc.) to the Arabian Sea, from China across the Pacific, from Australia over to the Indian Ocean, to cite the other major transport processes[7,8,25,41-44]. Since these particles are generated at the Earth's surface, they are mainly confined within the troposphere.

Carbonaceous aerosols

The major sources of carbonaceous aerosols are fossil fuel/biofuel combustion, biomass burning and the oxidation of biogenic and anthropogenic volatile organic compounds. They are broadly classified into BC and OC[45,46].

Black carbon: BC is produced primarily due to fossil fuel or biomass burning at low temperature and is mainly absorbing in nature[47]. Its absorption properties depend on the amount of graphitic carbon present (whether the result of complete or incomplete combustion). Being of fine size and chemically inert, BC particles can be transported from the source region to longer distances[48,49]. The BC aerosols mostly absorb radiation, thereby heating the layer in which they are present[5,50]. The atmospheric residence time of BC is of the order of a few weeks[4,48]. It has been suggested that BC warming might be second only to CO_2 and thereby complements global warming[51,52]. Studies also suggest that global warming due to BC can be as much as 0.3–0.4°C (ref. 53). Recent studies over the Indian sub-continent have debated the source of carbona-

ceous aerosols: fossil fuels[54–57] versus biofuels[58], whereas other studies[59] have shown that both fossil fuel and biofuel contribute equally to the carbonaceous aerosols over the Indian region.

Sources of BC vary by region. Some investigators have argued that fossil fuel and biofuel sources have significantly greater amounts of BC than scattering aerosols, making reductions of these sources particularly powerful mitigation strategies. However, this may not hold good for the Indian region because of the large organic carbon to black carbon (OC/BC) ratios reported from measurements[60]. Thus, extensive measurements and modelling studies need to be carried out before we can formulate BC reduction strategies. Recently, brown carbon resulting from biomass burning has attracted the global attention because of its significantly differing absorption properties, compared to BC[19]. Brown carbon absorbs strongly at the blue and ultra violet region, with very little absorption in the mid-visible. The largest sources of BC are Asia, Latin America and Africa. Some estimates show that China and India together account for 25–35% of global black carbon emissions. On a global basis, approximately 20% of BC is emitted from burning biofuels, 40% from fossil fuels and 40% from open biomass burning[61].

It is important to note that the lifetime of BC in the atmosphere is only a few days to weeks compared to CO_2, which has an atmospheric lifetime of more than 100 years. Even though BC absorbs at all wavelengths, its extinction coefficient is several orders of magnitude smaller (close to zero) at infrared wavelengths compared to visible wavelengths (Figure 2). Therefore, radiative effects of BC are mostly significant at visible wavelengths and not at infrared wavelengths. This is another major difference compared to CO_2. Thus, radiative impact of BC is different from that of greenhouse gases.

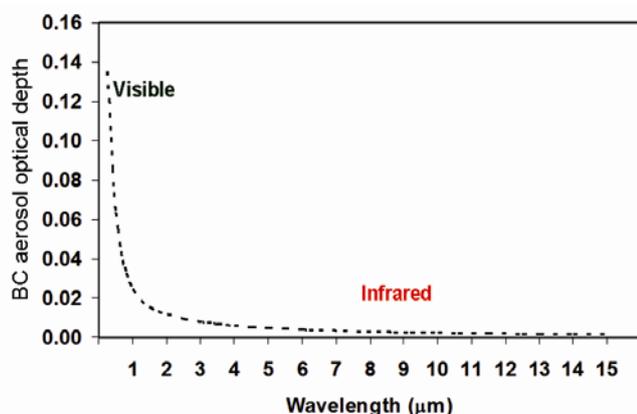*Organic carbon:* OC is one of the largest single components of biomass-burning aerosols. Therefore, it dominates

the carbonaceous aerosol emissions. The OC/BC ratio is used to trace their sources, and studies have shown that their ratio is greater than unity. In addition, they both have natural and anthropogenic sources. Unlike BC, OC mostly behaves like sulphate and thereby scatters radiation. Organic aerosol, unlike other species, is a collective term which refers to a large number of individual compounds[47]. Each individual compound has a different characteristic in terms of its radiative effect. Hundreds of different atmospheric organic compounds have been detected[62], making it extremely challenging to model their direct and indirect radiative effects[63]. Organic aerosols are emitted as primary aerosol particles and are also formed as secondary aerosol particles from the condensation of organic gases[24]. As they are volatile, their sampling is difficult compared to other species over India. This is one of the less understood aerosol species. Nevertheless, recent studies using aerosol mass spectrometers (AMS) have shown that organics are the major or dominant aerosol constituents throughout the anthropogenically influenced northern hemisphere[64].

Urban and rural aerosols: standard models

Hess *et al.*[65] based on comprehensive data collected from various locations have developed standard aerosol models, which are considered representative of a typical aerosol over various environments. They identified the major aerosol composites as continental clean, continental polluted, urban, desert, marine clean, marine polluted, etc. to describe a wide range of possible compositions. These components can be mixed together to form various aerosol mixtures. The mode radii (r_m), standard deviation (σ), density (ρ) and single scattering albedo (ω) (ratio of scattering to extinction) of the individual aerosol components are given in Table 2. The water-soluble part of aerosol particles originates from gas-to-particle conversion and consists of mainly sulphates and nitrates. The soot component is used to represent absorbing BC. Sea-salt represents aerosols generated from sea-water drops. Mineral dust aerosol or desert dust is produced in arid regions. Figure 3 shows the relative contribution of various aerosol species in rural and urban aerosol models (aerosol mass concentration is larger over the urban region by nearly a factor of 10). Substantially larger

Figure 2. Spectral variation of black carbon aerosol optical depth covering wavelengths from ultraviolet to infrared.

Table 2. Microphysical and optical properties of various aerosol components (based on data from Hess *et al.*[65])

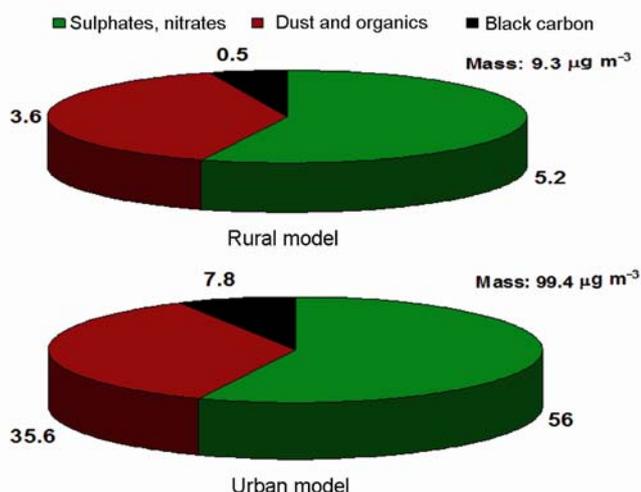| Aerosol component	r_m (μm)	σ	ρ (g cm^{-3})	ω
Sulphates, nitrates	0.029	2.24	1.8	0.99
Black carbon	0.018	2.0	1.0	0.23
Dust	0.39	2.0	2.6	0.83
Sea-salt (fine mode)	0.378	2.03	2.2	1.0
Sea-salt (coarse mode)	3.17	2.03	2.2	1.0

Figure 3. Rural and urban aerosol models (based on data from Hess *et al.*[65]).

abundance of BC aerosol mass concentration is an exclusive feature in the urban model.

Radiative impact of aerosols

The effect of atmospheric aerosols on climate due to their complex effects through different mechanisms is well recognized by the international community[13,66–68]. Effect of aerosols on the solar radiation can be broadly classified as direct impact and indirect impact. The direct radiative impact is due to the scattering and absorption of solar radiation by aerosols and produces climate forcing by changing the planetary albedo. The absorption and re-radiation of long-wave terrestrial radiation enhance the atmospheric greenhouse warming at the Earth's surface. Indirect radiative impact is due to the fact that aerosols can act as cloud condensation nuclei by providing surface area for water vapour condensation. An increase in the concentration of aerosols would result in an increase in number of cloud droplets, which in turn can increase the clouds albedo. This can cause a decrease in the short-wave solar radiation reaching the Earth's surface. Cloud albedo has a significant role in determining the global energy balance. This increases the cloud lifetime and inhibits precipitation.

The question of whether aerosols cool or warm the planet depends on the relative contribution of various chemical species which constitute the composite aerosol. An aerosol with significant BC content (absorbing type) can have net warming effect and complement to the greenhouse warming. On the other hand, an aerosol with significant sulphate content (scattering type) can have net cooling effect and partly offset the greenhouse warming. The knowledge of aerosol chemical composition is thus essential to make an accurate assessment of net warming/cooling effect of aerosols.

Several studies have suggested that aerosols may be mitigating global warming by increasing the planetary albedo, although the sign and magnitude of aerosol effects on climate are still uncertain. Compounding to the complexity of this problem is the interaction of aerosols with the clouds. Thus, it is important to gather information on aerosol microphysical properties and chemical composition from ground-based and aircraft platforms to carefully answer crucial questions related to the impact of aerosols on climate change.

There have been several reports on the impact of aerosols on climate. Some examples are: BC aerosols contribute to droughts and floods in China[69]; absorbing aerosols intensifies flooding and drought in India[70]; aerosol blocks sunlight and results in reduced crop yields[15], and so on. However, these results are not validated adequately and hence there are several issues to be considered before reaching conclusions on the impact of BC on climate. It is important to note that most of the chemistry-transport model predictions of aerosol chemical characteristics, in general, and BC aerosols in particular, over India are unrealistic. In addition, many models still assume BC as an independent aerosol species (externally mixed).

Recent studies have revealed that deposition of aerosol BC on snow can reduce the snow albedo, leading to enhanced absorption of solar radiation and hence faster melting rates of glaciers. Several other studies report that enhanced warming due to aerosol BC at higher levels is responsible for the faster melting of glaciers. However, in the Himalayas, systematic studies to understand the influence of aerosols on snow/glacier albedo are not yet available.

Aerosol chemistry over India: current status

It is now well known that aerosols are one of the most important trace components of the Earth's atmosphere and are of immense scientific interest due to their complex nature and consequent effects on the climate. Due to their high heterogeneity both spatially and temporally, several field campaigns have been undertaken at the national level in the recent years to improve the understanding of the optical, physical and chemical properties of aerosols and their radiative impacts. The major goals of these experiments have been the characterization of regional aerosol properties, their controlling processes and estimation of their direct and indirect radiative forcing. In India, systematic studies of the physico-chemical properties of aerosols, their temporal heterogeneities, spectral characteristics, size distribution and modulation of their properties by regional mesoscale and synoptic meteorological processes have been carried out extensively since the 1980s at different distinct geographical regions as part of the different national programmes such as the IMAP and later under ISRO–GBP.

Over continental India

Sharma and Patil[71] collected aerosol samples from an industrialized part of Mumbai. These were analysed for 27 chemical species. Size-segregated measurements of F, Cl, NO$_3$, SO$_4$, Na, K, Ca, Mg and NH$_4$ in aerosols were made in Agra city during December 1992–March 1993 (ref. 72). Except for NH$_4$, Cl and Na, all components were found to have a bimodal distribution. It was observed that the fine fraction was dominated by NH$_4$, K, NO$_3$ and SO$_4$, whereas Na, Ca, Mg, F and Cl contributed to the coarse fraction. Major observation was that 58% of SO$_4$ and 67% of NO$_3$ contribute to fine mode and the coarse mode comprised 42% and 33% of SO$_4$ and NO$_3$ respectively.

A road/land campaign (LC-I) was conducted during February–March 2004 under ISRO–GBP, to understand the spatial distribution of aerosols and trace gases over Central/peninsular India. Simultaneous measurements were made over spatially separated locations, using identical instruments. These measurements covered an area of more than million square kilometre over the course of a month from land-based mobile laboratories, and generated a wealth of information on BC as well as important aerosol parameters, including size, mass concentration, optical depth, and scattering and absorption coefficients using state-of-the-art instruments. Details of these campaigns and the major findings have been reported in the literature[73–75]. Nair et al.[76] made chemical composition measurements during LC-I and compared them with those made over oceanic regions. Chemical composition of coastal aerosol is expected to be a mixture of continental and marine species. George et al.[77] reported annual mean aerosol mass loading of 54 µg m^{-3} based on measurements of chemical composition at the tropical coastal location, Thiruvananthapuram. The chemical analysis of samples revealed the presence of Cl, SO$_4$ and NO$_3$ as major anionic species, and Na, NH$_4$, Fe and Ca as the major cationic species. It was found that ions like Na, Cl, Mg and K are mainly of oceanic origin and showed a peak during monsoon season, and SO$_4$, NH$_4$, PO$_4$, Fe, Al and trace elements exhibited a peak in winter/summer. Safai et al.[78] reported that concentrations of SO$_4$, NO$_3$, NH$_4$ and BC aerosols increased by 4, 2, 3.5 and 1.7 times respectively, during foggy/hazy days based on measurements at Agra. It was found that aerosols are acidic during intense foggy/hazy days, but the fog water showed alkaline nature and attributed to the neutralizing capacity of NH$_4$ aerosols. Rastogi and Sarin[79], based on measurements from several field campaigns, pointed out that observed concentrations of BC and OC are significantly lower than those reported for the metro cities in South Asia, but the OC/BC ratios (4.3 to 35 with an average of 8.3) are significantly higher than the characteristic ratio (2–4) for a typical urban atmosphere. This inference has importance while assessing mitigation strategies for aerosol black carbon.

National Land Campaign II (LC-II) was organized by the Indian Space Research Organization under ISRO–GBP during December 2004, to characterize the regional aerosol properties and trace gases across the entire Indo-Gangetic belt. The campaign provided a comprehensive database on the optical, microphysical and chemical properties of aerosols over the Indo-Gangetic belt[80–83]. All these studies showed the persistence of high aerosol optical depth and BC concentrations near the surface[84]. Kulshrestha et al.[85] studied the secondary aerosol formation at Allahabad in the Indo-Gangetic region during LC-II. They used Potential Source Contribution Function (PSCF analysis) to identify regional source locations of the ionic species. The average concentration of water-soluble inorganic ions (sum of anions and cations) was 63.2 µg m^{-3}. The NO$_3$, SO$_4$ (15.8 µg m^{-3}) and NH$_4$ concentrations contributed about 87% of the total mass of water-soluble aerosol species. They measured aerosols at urban and rural sites near Agra as well[85].

The ratio of OC to BC is an important factor determining radiative impact of aerosols. Ram and Sarin[86] measured the atmospheric abundances of BC, OC and water-soluble organic carbon (WSOC) during winter from urban and rural locations in northern India. They observed dominant contribution from biomass burning sources (wood-fuel and agriculture waste) at the urban sites with OC/BC ratios in the range 2.4–14.5 in contrast to the OC/BC ratios at the rural site (2.1–4.0) influenced by emissions from coal-fired industries. They concluded that comprehensive measurements of BC, OC and WSOC/OC ratios from northern India are crucial in modelling climate impact of carbonaceous aerosols on a regional scale. Behera and Sharma[87] also analysed aerosol samples collected from Kanpur for ionic species (NH$_4$, SO$_4$, NO$_3$ and Cl), carbon contents and elemental contents (Ca, Mg, Na, K, Al, Si, Fe, Ti, Mn, V, Cr, Ni, Zn, Cd, Pb, Cu, As and Se). Based on a mass reconstruction approach they differentiated primary and secondary components of measured aerosol and established that secondary aerosol formation (inorganic and organic) was responsible for significant mass of aerosol (approximately 50%). Atmospheric aerosols were collected at a semi-urban site in Pune city, located in the southwestern part of India, during 2007–08 covering different seasons[88]. Chemical analysis of aerosols collected over Pune showed that anthropogenic aerosols (SO$_4$, Cl, K, Ca and Mg together with NO$_3$, NH$_4$, Cu, Zn and black carbon) contributed 73% of the total aerosol mass. Rengarajan et al.[89] have studied chemical composition of PM2.5 over an urban site in a semi-arid region of western India during winter. The concentration of PM2.5 ranged from 32 to 106 µg m^{-3}, in which carbonaceous (BC and OC) and water-soluble inorganic constituents contributed 58% and 29% respectively. They presented evidence for the significant role of secondary organic aerosol (SOA) in an urban environment by reporting a ratio of water-soluble to particulate OC in the range 0.26–0.52.

Ram and Sarin[86] measured BC, OC, WSOC and inorganic ions at an urban site, Kanpur in northern India. They presented evidence for the secondary aerosol formation and substantial variability in the composition of particulate matter. The analysis of chemical composition indicates that carbonaceous aerosols and water-soluble inorganic species account for nearly 50% and 20% of the PM2.5 mass respectively. Correlation analysis of BC and OC indicates that biomass burning is a dominant source. The average WSOC/OC ratio was found to be high in the daytime samples compared to those in the night-time samples. This indicates increased contribution of secondary organic aerosols during night.

Over oceans

The Indian Ocean Experiment (INDOEX) was an international field campaign for the Indian Ocean. Nair et al.[90] studied cations such as Na, K, Mg, Mn, Zn, Fe, Cu and Pb and anions like Cl, SO_4 and NO_3 based on aerosol samples collected from the Arabian Sea and Indian Ocean. Surprisingly, near the coastal regions only up to 40% of the total mass collected could be accounted by these ions, whereas over the open sea, including the ITCZ region 50–70% of the mass could be quantified.

The Integrated Campaign for Aerosols, gases and Radiation Budget (ICARB) was a multi-institutional, multi-instrumental, multi-platform field campaign, where integrated observation and measurements of aerosols with special emphasis on BC, radiation and trace gases along with other complementary measurements on boundary layers and meteorological parameters were made simultaneously[7]. The main goal of the ICARB was to assess the regional radiative impact of aerosols and trace gases, and to quantify the effect of the long-range transport of aerosols and trace gases, involving the Indian mainland, the Arabian Sea, the Bay of Bengal (BoB), and tropical Indian Ocean during February–May 2006. During the ICARB field campaign, George and Nair[91] studied chemical composition of aerosols over the Arabian Sea. They found that SO_4, Cl and Na are the major ionic species present. Apart from these, other dominating, water-soluble components of aerosols are NO_3 and Ca. They concluded that non-sea-salt component dominates and accounts for 76% of the total aerosol mass over the Arabian Sea.

Earlier studies have shown transport of substantial amount of dust from continental India to adjacent oceans. Kumar et al.[92] studied the factors controlling the spatiotemporal variability in the fractional solubility of aerosol iron over the BoB based on measurements of chemical composition and using back-trajectory analysis. They have identified continental outflow from the two major source regions, namely outflow from the Indo-Gangetic Plains (IGP) and South East Asian outflow over south

BoB. These workers provided evidence for the acid processing of mineral dust during atmospheric transport from IGP by demonstrating a linear relationship between fractional Fe solubility and nss-SO_4. In contrast, a temporal shift in the winds, representing the outflow from South East Asia and aerosol composition over south BoB, exhibited enhanced fractional solubility of aerosol Fe associated with the lower abundance of dust and nss-SO_4. These observations indicate the dominance of combustion sources (biomass burning and fossil-fuel) in dictating the aerosol iron solubility over south BoB. Das et al.[93] measured suspended particulate matter over BoB and reported mass concentration of 39 $\mu g\ m^{-3}$. They found that Na and SO_4 were the most dominant water-soluble constituents over BoB. They used intra-correlation analysis to show that Na and Cl were well correlated, and SO_4–Ca^+ and SO_4–NH_4 were poorly correlated. This indicates that these ion pairs are probably derived from different sources.

High-altitude sites

The first long-term measurements of aerosol chemical composition were made by Ram et al.[94] at Manora Peak (1950 m amsl), a high-altitude site in the central Himalayas. They reported that mass concentration of composite aerosols varied from 13 to 272 $\mu g\ m^{-3}$ over this region. Aerosol mass was observed to increase significantly during summer (April–June) due to increase in the concentration of mineral dust associated with the long-range transport from desert regions (from the Middle East and Thar Desert in western India). A significant seasonal variability in the carbonaceous species was also reported with lower concentration during the summer and monsoon (July–August) and relatively high concentration during the post-monsoon (September–November) and winter (December–March). On the average, total carbonaceous aerosols and water-soluble inorganic species contributed nearly 25% and 10% of the aerosol mass respectively.

Darjeeling is a high-altitude location (2200 m amsl) in the northeastern Himalayas. Chatterjee et al.[95] by recognizing the urgent need for an improved understanding of the atmospheric aerosol initiated an extensive aerosol sampling programme at this location. The average concentrations of fine and coarse mode aerosol were found to be 29.5 and 19.6 $\mu g\ m^{-3}$ respectively. These studies revealed that gas-phase photochemical oxidation of SO_2 during pre-monsoon and aqueous-phase oxidation during winter and post-monsoon were the major pathways for the formation of SO_4 in the atmosphere.

Mount Abu (1680 m amsl) is another high-altitude site in western India. Rastogi and Sarin[96], and Kumar and Sarin[97,98] have made measurements of chemical composition at Mount Abu and reported the presence of water-soluble ionic species (Na, NH_4, K, Mg, Ca, Cl, NO_3, SO_4, and HCO_3) in aerosols. They found that water-soluble

ionic composition constitutes 50%, 39% and 31% of the aerosol PM2.5 mass during winter, summer and monsoon respectively, with dominant contribution from SO_4, NH_4 and HCO_3. Their studies indicate long-range transport of combustion products (biomass burning and fossil-fuel emissions) from northern India. They observed relatively high abundance of nitrate in the coarse mode during all seasons, indicating its association with mineral dust.

In summary, it appears that information on aerosol chemical composition is not adequate to develop a comprehensive aerosol model for India. However, Ram and Sarin[86] have made efforts in characterizing OC/BC ratios over a few locations in India. It is known that OC/BC ratio is less than 1.0 in the case of diesel exhaust, whereas that from wood smoke is much larger than 1.0 (Figure 4). Studies over the Indian region show that the OC/BC ratio is much larger than 1.0 (ranges from 3 to 15, Figure 5)[86,94]. They reported large OC/BC ratios in the range 2.4–14.5. This indicates a dominant contribution from biomass burning sources. Such large OC/BC ratios are observed over China as well. Thus it appears that at least over South Asia, the conclusion that heating by BC and cooling by OC cancel out each other may not hold good.

Aerosol chemical model for India

As discussed earlier, a comprehensive data on aerosol chemistry is still unavailable over India. Most of the available measurements are made as part of national field campaigns or at fixed sites and are limited to a certain period or location due to their specific goals. This limited information is inadequate to develop an aerosol chemistry model for India, especially for addressing to climate change issues.
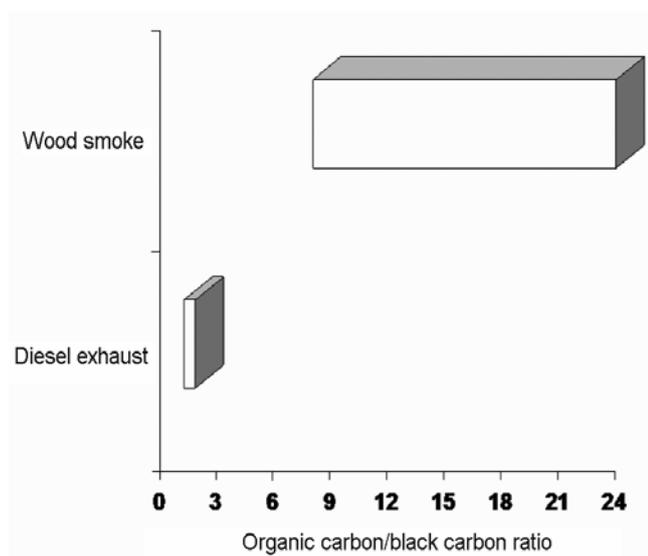
Satheesh and Srinivasan[99] proposed a novel means to develop aerosol chemistry models at locations where detailed aerosol characterization is not available. This method can be used to derive aerosol chemistry models that are 'optically' equivalent and can be used as input to Mie scattering or radtaive transfer models to simulate the observed aerosol optical properties and radiative fluxes. This method utilizes spectral optical depths and black carbon aerosol mass concentration as input. Here, we present an aerosol chemistry model for India following this approach. First, we make an initial assumption of the aerosol composition (zero order). The assumed initial composition has no impact on the final result, but minimizes the number of iterations required. We rely on aerosol models of Hess et al.[65] as zero order assumption. The model of Hess et al.[65] was developed based on comprehensive data over a much broader area and hence representative of a typical aerosol over various environments. They identified the major aerosol composites as continental clean, continental polluted, urban, desert, marine clean, marine polluted, etc. To describe a wide range of possible aerosol compositions, Hess et al.[65] modelled aerosols as various components, each of them meant to be representative for a certain origin. These components can be mixed together to form various aerosol mixtures (such as continental clean, marine polluted, etc.). The mode radii (r_m), standard deviation (σ), density (ρ), and single scattering albedo (ω) of the individual aerosol components are given in Table 2. The water-soluble part of aerosol particles originates from gas-to-particle conversion and consists of mainly sulphates and nitrates. The soot component is used to represent absorbing BC. Sea-salt represents aerosols generated from sea-water drops. Mineral dust aerosol or desert dust is produced in arid regions.
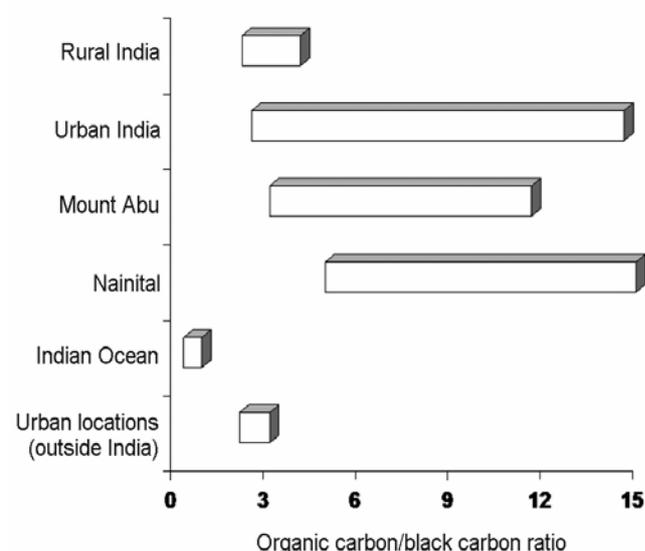

Figure 4. Organic carbon/black carbon ratio for wood smoke and diesel exhaust (values from Satheesh et al.[49]).

Figure 5. Organic carbon/black carbon ratio observed over various locations in India (values from Ram and Sarin[86]).

Spectral optical depths (extinction coefficient integrated over a vertical atmospheric column of unit cross-section) and BC mass concentration are being measured as part of ARFINET observatories and are reported in several published papers available in the literature. Aerosol chemical model ('optically' equivalent model) developed using ARFINET database and following the approach described in Satheesh and Srinivasan[99] is shown in Figure 6. During winter scattering aerosols such as sulphates and nitrates are dominant, and during summer dust is the dominant species.

State of mixing of aerosols

There has been a substantial increase in interest in the climate impact of BC aerosols due to their high absorption characteristics, which in turn depend on their production mechanism (whether result of complete burning or not). In addition to exerting its own radiative impact, BC aerosol can substantially contaminate other aerosol species and also can get contaminated by other species thereby altering the radiative properties of the entire, aerosol system and its ability to act as cloud condensation nuclei. An aerosol system with individual aerosol species existing independently is known as externally mixed aerosol, whereas in internally mixed state each particle contains several species. Often large particles such as dust are coated with small aerosols such as BC. Due to the complex state of mixing, there is still a great degree of uncertainty about the hygroscopic properties of BC particles and hence their role as cloud condensation
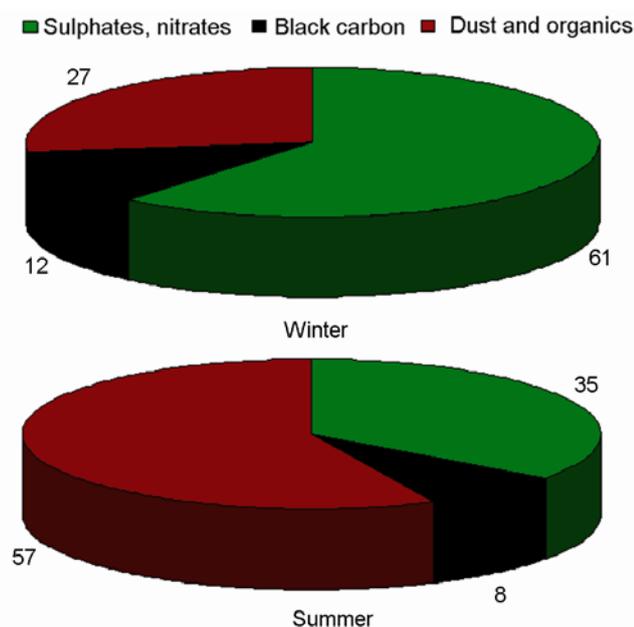

Figure 6. Aerosol chemistry ('optically' equivalent) model for India. Percentage contribution of various aerosol species is in terms of optical depth.

nuclei. In the atmosphere, BC particles interact with other aerosol particles and gas-phase species, and exist mixed with organic and inorganic particles at various states of mixing. Hygroscopic properties of aerosols containing BC mixed with hydrophilic and hydrophobic compounds at various mixing states have now become important topics of research. Recent studies have shown that when sulphate or organics is coated over BC aerosols, its absorption effects are enhanced significantly. In case of BC mixed with large dust particles, absorption of the composite dust–BC system is enhanced by a factor of two to three compared to the sum of BC and dust absorption[100]. Moffet and Prather[101] carried out *in situ* measurements of the size resolved mixing state, optical properties and ageing timescales for soot particles and found that, immediately after sunrise, soot particles begin to develop a coating of secondary species, including sulphate, ammonium, organics, nitrate and water. These direct measurements suggest a maximum absorption enhancement of 1.6 over fresh soot because of mixing. Such observations explain the higher measured soot forcing compared to the models[102]. Aerosol microphysics, chemical composition and cloud condensation nuclei concentrations were measured at the Mexico City during Megacity Initiative: Local and Global Research Observations (MILAGRO) in March 2006 (ref. 103). The study suggests mixing of nonhygroscopic primary organic aerosol (POA) and BC with photo-chemically produced hygroscopic species, and thereby the increase of their hygroscopicity parameter to 0.1 take place in a few hours during daytime. The rapid mixing also indicates that at least for very active photo-chemical environments such as Mexico City, the timescale during daytime for the conversion of hydrophobic POA and BC to hydrophilic particles is substantially shorter than the 1–2 days used in some global models. The conversion timescale is substantially longer during night.

Pratt and Prather[104] measured vertical profiles of size-resolved aerosol mixing state over Wyoming. In general, biomass burning, OC and soot particles were found frequently internally mixed with ammonium, nitrate and sulphate at lower altitudes. Internally mixed aerosol particles consisting of one or more hygroscopic compounds can contain aerosols in both solid and liquid phase. The solid-to-liquid transition of such mixed aerosols as the RH increases influences their light-scattering properties through changes in particle shape, size and refractive index. Using laboratory experiments, Freney *et al.*[105] have shown that solid inclusions inside aqueous droplets even at high RH values are likely. This indicates that estimation of radiative effects of such aerosols needs to account for such scenarios. Wex *et al.*[106] examined the range of particle hygroscopicities that occurs in the atmosphere, based on the literature data of measured hygroscopic growth or based on chemical composition. They observed that when all aerosol species in the

mixture are hygroscopic, the composite aerosol is often similar as an external mixture with respect to hygroscopicity. Though there have been a few localized studies on the state of mixing of aerosols, information on the realistic aerosol state of mixing (which is most important in determining their hygroscopic properties as well as radiative impact) on a regional or global scale is not yet available.

Environmental impact of BC aerosols

Various field campaigns over India revealed that the range of BC mass concentrations varies from 1 μg m^{-3} to as high as 16 μg m^{-3}. In this section, we examine some side effects of the presence of large BC mass concentrations over the Asian region from the climate perspective. There have been proposals to consider geoengineering as an option to deliberately manipulate the Earth's climate to counteract the effects of global warming from greenhouse gas emissions[107–109]. These include direct methods (e.g. CO_2 air capture) and indirect methods (e.g. iron fertilization of oceans). Solar radiation management techniques (e.g. stratospheric sulphur aerosols) do not reduce greenhouse gas concentrations, but can only address the warming effects of CO_2 and other gases[110]. These techniques cannot address problems such as ocean acidification, which are expected as a result for rising CO_2 levels. Examples of proposed solar radiation management techniques include placing space mirrors, injection of stratospheric sulphur aerosols and cloud reflectivity enhancement. Most techniques have at least some side effects. One low-cost proposal is to paint pavements and roof materials in white or pale colours to reflect solar radiation back to space[111–114]. This is a benign technique, although limited in its ultimate effectiveness by the constrained surface area available for treatment. Even though cooling as a result of this method is smaller when compared to the 3.7 W m^{-2} of positive forcing from a doubling of CO_2, it can be achieved at little or no cost by simply selecting different materials. Further, it can reduce the need for air conditioning, which causes CO_2 emissions which worsen global warming.

One of the major issues overlooked in such proposal is the effect of surface reflectance in atmospheric absorption due to aerosols and consequent aerosol-induced warming. Recent studies over the Indian region have shown that irrespective of the comparatively small percentage contribution in optical depth (10–20), aerosol BC has an important role in the overall absorption and hence warming of the lower atmosphere. When the amount of absorbing aerosols such as BC is significant, the reflectance of the underlying surface plays an important role. This is particularly important to note that aerosol BC mass concentration over India and China is of the order of 10–20 μg m^{-3}, which is quite large.

Recent experiments using wide-ranging multi-platform instruments conducted India show that most of the region is characterized by elevated aerosol layers[115,116], and a substantial fraction (as much as 50–70%) of aerosol optical depth was found contributed by aerosols above the surface (located around 2–3 km). We have made sensitivity studies using radiative transfer models to test the effect of whitening rooftops in the presence of absorbing aerosol BC. The key parameters in determining direct radiative forcing such as aerosol optical properties, aerosol optical depth, the single scattering albedo (which is a measure of whether a particular species scatters or absorbs radiation) and scattering phase function are obtained from the urban aerosol model described in Hess et al.[65], as input to radiative transfer model. A summary of the sensitivity study is shown in Figure 7. For the same urban aerosol, we found that aerosol-induced lower atmospheric warming increased from 0.7 to 2.3 K/day as a consequence of whitening rooftops.

Our study demonstrates that if we whiten the rooftops over regions where aerosol is dominated by BC, aerosol-induced warming increases dramatically. Thus, it is obvious that an accurate knowledge of aerosol chemistry is essential for assessment of the environmental impact of such schemes. Extensive modelling studies should be carried out before implementing such schemes over India to avert any catastrophe due to unexpected warming effects of absorbing aerosols.

Mitigation of black carbon aerosols

Of late there is a tendency to project mitigation of BC aerosols as a quick solution to climate change[52]. However, some studies show that drastic decrease in BC aerosols will result in an increase in surface temperature[117]. Thus, removal of BC will lead to sudden change in warming/cooling patterns. As mentioned earlier, the question of whether aerosols cool or warm the planet depends on the relative contribution of various chemical species which constitute the aerosols. An aerosol with significant BC content can have net warming effect and complement the greenhouse warming. Reports have shown that the heating by BC is mostly offset due to cooling by sulphate aerosols[24]. Thus, it appears that the net effect is cooling by organic aerosols. It is known that OC/BC ratio is less than 1.0 in the case of diesel exhaust whereas that from wood smoke is much larger than 1.0 (Figure 7). Studies over the Indian region show that OC/BC ratio is much larger than 1.0 (ranges from 3–15)[86,94]. Thus it is important to note that since BC and OC are derived from the same source, mitigation strategies targeting BC will lead to reduction of OC as well.

There are two aspects to be addressed while discussing radiative impact of BC. While BC is the major aerosol species which absorbs light, scattering due to BC and all
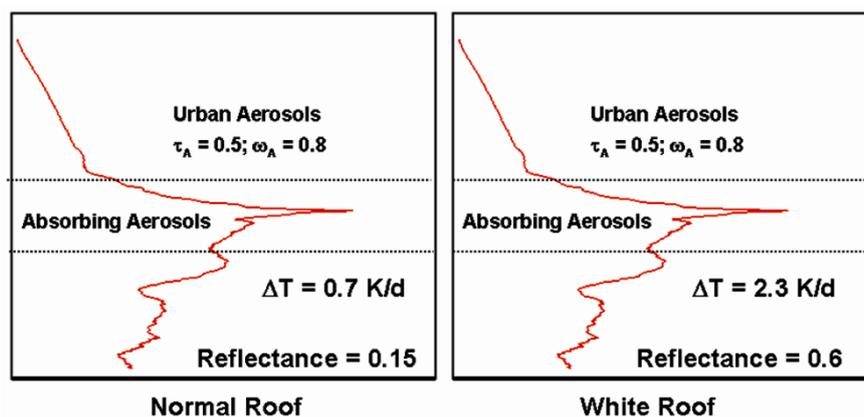
Figure 7. Sensitivity study showing enhanced warming as a result of whitening roofs. Urban aerosol model is assumed in this sensitivity analysis.
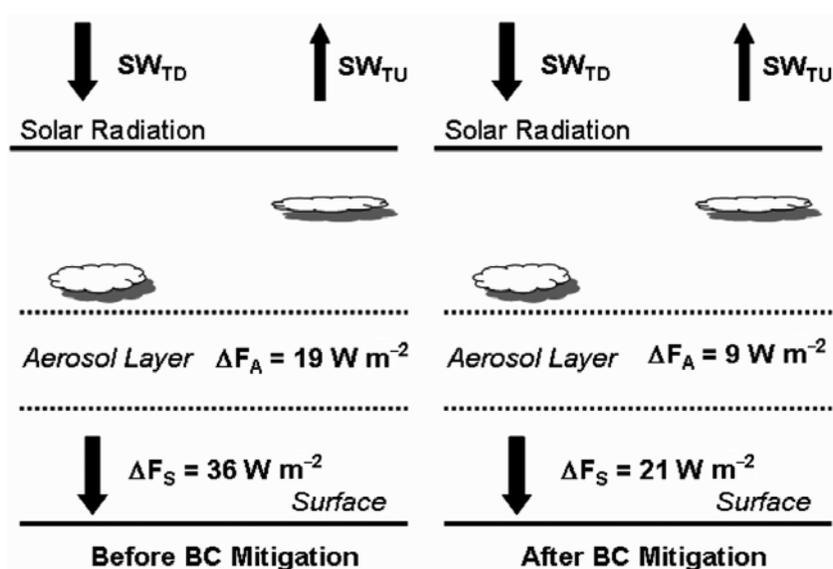

Figure 8. Sensitivity study showing the consequence of mitigation of BC to atmospheric warming and surface cooling.

other scattering aerosol species lead to cooling of the Earth's surface. If an aerosol consists of BC, it can warm the atmosphere due to its short-wave absorption, but simultaneously it cools the Earth's surface by reducing the incoming solar radiation. Atmospheric temperature decrease due to this surface dimming is larger than atmospheric warming by BC. Thus, reduction of BC may lead to reduction of surface cooling and may lead to an increase in atmospheric warming.

Novakov et al.[117] have shown using data over California that reduction of BC has led to further warming. This aspect needs to be studied before attempting any BC reduction strategies. We have made a sensitivity study using radiation models. Aerosol optical properties from the urban aerosol model were used as input in the radiation model to estimate atmospheric warming and surface cooling. The exercise was repeated by removing BC from the model. Summary of the results is shown in Figure 8. While atmospheric warming was reduced by 10 W m^{-2} as

a result of removal of BC, surface cooling was reduced by a larger amount, 15 W m^{-2}. Thus, removal of BC lead is to reduction of BC-induced atmospheric warming, but at the same time enhances surface warming by a larger amount. It is possible that a drastic decrease in BC aerosols may result in an increase in surface temperature by several degrees. Consequences associated with such a reduction in BC should be assessed accurately and adequately before it is implemented to mitigate climate change. Therefore, at least over regions where OC is abundant, reduction of BC may not be a viable option to mitigate warming.

Summary

The information on aerosol chemical composition over India is available from a few measurements as part of the national field campaigns or as part of fixed sites. The database is not adequate to develop a comprehensive

aerosol model for India. Studies over the Indian region show that OC/BC ratio is much larger than 1.0 and ranges from 3 to 15. This indicates a dominant contribution from biomass burning sources as it is known that OC/BC ratio is less than 1.0 in the case of diesel. It appears that at least over South Asia, understanding that heating by BC and cooling by OC cancel out each other may not hold. Scarcity of nation-wide information on aerosol chemical composition including volatile organic compounds, and their vertical distribution demands a national effort in this direction. Establishment of a network of AMS nation-wide may be an option to address these issues and thereby to carefully answer crucial questions related to the role of aerosol chemistry on regional climate. Recently, the Ministry of Environment and Forests (MoEF), Government of India launched a National Carbonaceous Aerosol Programme (NCAP), to monitor key aerosol parameters by augmenting the ARFINET observatories. This provides a platform for such AMS network. Sensitivity studies show that because of the large OC/BC ratio over India, reduction of BC may not be a feasible option to mitigate warming. No doubt, there is still a great degree of uncertainty about the role of aerosol chemistry on regional climate.

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