

## Atmospheric carbonaceous aerosols: issues, radiative forcing and climate impacts

*S. Ramachandran, R. Rengarajan and M. M. Sarin*

Atmospheric aerosols (a mixture of solid or liquid particles suspended in the air medium) are short-lived, with a residence time of about a week in the lower troposphere. Unlike the principal greenhouse gases, aerosols are more concentrated in the source regions and exhibit strong spatial and temporal variations. The characteristic primary or direct sources of aerosols include the world oceans (sea salt particles), arid and semi-arid regions (wind-blown soil dust), terrestrial biota (biological material of plant origin) and smoke from forest fires. In addition, there are direct sources from land-use changes, anthropogenic emissions (e.g. soot, smoke, road dust, etc.), terrestrial ejecta (volcanic effluvia) and meteorites (extraterrestrial and interplanetary dust). The secondary or indirect sources contribute particles below 1  $\mu\text{m}$  via conversion of the natural and manmade atmospheric trace gases into solid and liquid particles. This process, known as gas-to-particle conversion mechanism, depends on a number of precursors which include sulphur and nitrogen-bearing gases among others. The major aerosol species present in the atmosphere include sea salt, mineral dust, sulphate, black carbon organic carbon and nitrate.

Global climate is influenced by natural and manmade processes such as the variation in the output of the sun, changes in the atmospheric composition and alteration of surface reflectance characteristics by land use<sup>1</sup>. The influence on climate by different agents is evaluated by radiative forcing which is expressed in Watts per square metre ( $\text{Wm}^{-2}$ ). Radiative forcing can be defined as the influence a species has in altering the balance of the incoming and the outgoing energy of the earth-atmosphere system. Thus, radiative forcing is a measure by which one can assess and compare the manmade and natural drivers of climate change<sup>1</sup>. The radiative forcing for all greenhouse gases relative to the beginning of the industrial era is positive as each gas absorbs the infrared radiation in the atmosphere. Increase in carbon dioxide concentrations among the greenhouse gases has caused the largest atmospheric

warming (positive forcing). Tropospheric ozone increase has resulted in warming while stratospheric ozone decrease has produced cooling<sup>1</sup>.

Atmospheric aerosols are gaining considerable importance in the present-day scenario of growing anthropogenic activities as well as in terms of their direct/indirect effects on climate. The direct radiative effects of aerosols involve both scattering and absorption of solar radiation, and the relative importance of these processes depends on their chemical composition, refractive index and size distribution. The atmospheric radiative forcing is calculated as the difference between top of the atmosphere and surface forcings, and refers to the amount of energy trapped within the atmosphere. Both scattering and absorbing type particles produce cooling at the earth's surface, while their effects in the atmosphere vary with altitude. For scattering particles (e.g. sulphate), the top of the atmosphere forcing is almost similar to the surface forcing; while the surface forcing is about 2–3 times larger than the top of the atmosphere forcing for absorbing aerosols (e.g. black carbon) and, thus, absorbing aerosols produce a large atmospheric warming. The greenhouse gases are globally well mixed and their radiative effects are homogeneous and one of warming. In contrast, aerosols exhibit regional signatures and act to either warm or cool the atmosphere. Although the aerosols exist in abundance near source regions, they impact global climate as their radiative influence can get transported due to changes in the mean atmospheric circulation patterns. In addition, the forcing due to aerosols is greatest during daytime and in summer, whereas greenhouse gas forcing acts over the full diurnal and seasonal cycles and hence aerosols perturb the earth's radiation budget differently than greenhouse gases in many important ways<sup>2</sup>.

Cloud droplets are formed in the lower atmosphere by condensation of water on existing aerosol particles. Sulphate and organic carbon, being water soluble, act as good cloud condensation nuclei (CCN). Thus the concentration, size and compo-

sition of the aerosols that can act as cloud condensation nuclei determine the cloud properties, evolution and development of precipitation. Aerosols may also play a role in the formation of ice nuclei in clouds. The indirect radiative effects of aerosols are more uncertain than the direct radiative effects of aerosols<sup>1</sup>. The indirect effects of aerosols on clouds and precipitation occur in the following ways: (a) aerosols can increase the lifetime of clouds and reflectivity (albedo), thereby decreasing the precipitation and radiation reaching the surface of the earth, (b) aerosols can absorb the solar radiation, re-emit as thermal radiation and by heating the air mass may cause evaporation of cloud droplets, and (c) an increase in the ice nuclei can increase the precipitation efficiency of clouds. Recent studies have indicated that large concentrations of manmade aerosols can lead to both decrease and increase of rainfall as a result of their radiative and CCN properties. For example, pristine tropical clouds with low CCN concentrations rain out too quickly, while in heavily polluted clouds much of the water can evaporate before precipitating because of aerosol absorption<sup>3</sup>.

In this context, sulphate and carbonaceous aerosols (elemental carbon (EC), also known as black carbon (BC) and organic carbon (OC)) are of major interest as their atmospheric abundances have substantially increased from pre-industrial times to the present-day. As the aerosols are concentrated near the source regions, the atmospheric warming can be about an order of magnitude higher than the atmospheric warming produced due to greenhouse gases over the aerosol-source regions<sup>3,4</sup>. More importantly, apart from their climatic impact, carbonaceous aerosols when mixed with the atmospheric dust have potential to influence the atmospheric chemistry of several trace gases. Dinitrogen pentoxide ( $\text{N}_2\text{O}_5$ ), ozone ( $\text{O}_3$ ) and hydroperoxyl ( $\text{HO}_2$ ) radicals through heterogeneous chemical reactions with dust can affect the photochemical oxidant cycle and decrease ozone concentrations by 10% in as well as nearby dust-source regions<sup>5</sup>.

The carbonaceous aerosols are the single largest absorber of solar radiation. The radiative forcing at the top of the atmosphere is found to change sign from negative to positive when carbonaceous aerosols are abundant over higher reflecting surfaces such as land and snow. The downward radiation flux decreases further when absorbing aerosols are abundant in the atmosphere which results in a higher atmospheric heating. The radiative forcing at the top of the atmosphere changes sign over higher reflectance surfaces (e.g. land, snow) as the radiation reflected from the surface below would again interact with absorbing aerosols. Thus a higher carbonaceous aerosol loading over land can exert a significant influence in terms of climate change than over the oceans. A recent study suggests that the atmospheric warming trend by aerosols over Asia can have substantial implications for the elevated regions of Himalaya, where the warming of about 0.15–0.3 K per decade during the past several decades has led to the reduction of glacier mass<sup>6,7</sup>. It is also reported that the industrial black carbon emissions in the 20th century may have altered the Arctic climate forcing<sup>8</sup>.

Among the carbonaceous species, EC has a chemical structure identical to impure graphite. EC is generated by the combustion of carbon-containing fossil fuels and biomass burning. Numerous studies in the literature have shown that carbonaceous species are major contributor to the aerosol mass concentration smaller than 2.5 micron size in aerodynamic diameter (PM<sub>2.5</sub>). The combustion particles containing EC with variable amounts of OC and trace metals (i.e. soot) consist of about 50 nm diameter particles, agglomerated in chains (Figure 1). The phases of aerosols (e.g. aqueous or crystalline) affect their roles in atmospheric processes. The organic compounds are hygroscopic and cool the atmosphere as they are scatterers. They can also serve as cloud condensation nuclei. In contrast, EC particles are hydrophobic and absorb solar radiation.

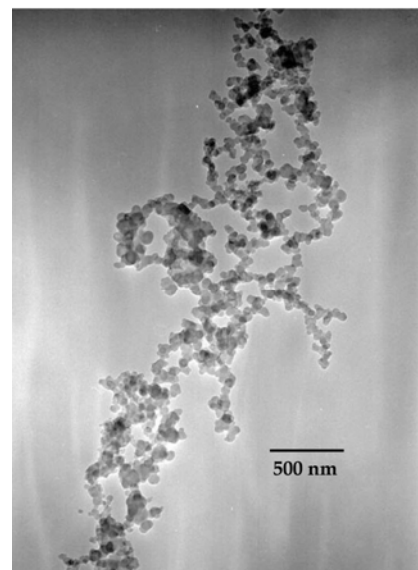
In the lower atmosphere, the dominant cycling of carbonaceous particles between hydrophilic and hydrophobic states with relative humidity (RH) changes is gaining considerable importance in the context of atmospheric reactions, wherein EC is being used as a surrogate for soot particles. The reaction of soot with ozone

and nitrogen oxides (NO and NO<sub>2</sub>) is of particular interest in terms of air pollutants. A most significant reaction involving EC is the conversion of nitrogen dioxide (NO<sub>2</sub>) to nitrous acid (HONO) and smaller amounts of nitric oxide (NO)<sup>9</sup>:



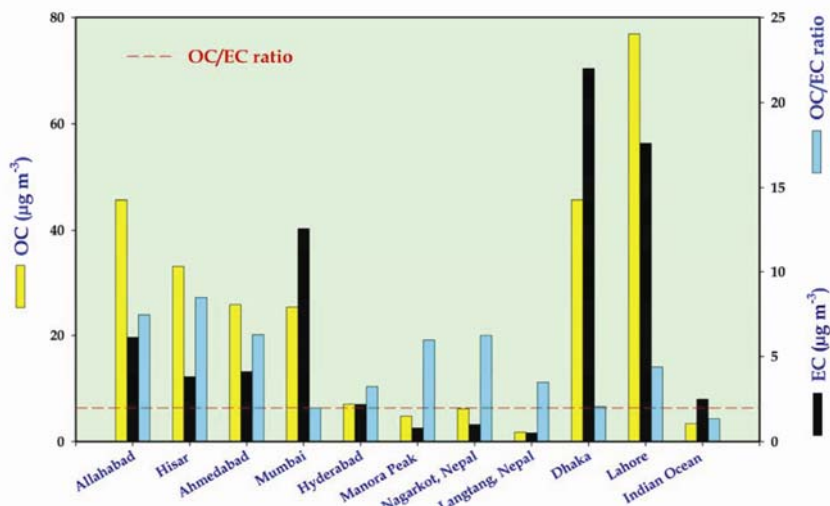
This reaction is of interest because current models underestimate the production of HONO, which is an important photolytic source of hydroxyl radical. This reaction could also be important as a reduction step for atmospheric nitrogen species, in contrast to other atmospheric reactions which tend to oxidize trace gases (SO<sub>2</sub> to H<sub>2</sub>SO<sub>4</sub>). It appears that the formation of NO results from the secondary reaction of HONO at the surface of the soot. A number of other atmospheric gases also react with soot. As an example, ozone is destroyed on soot to form O<sub>2</sub>, CO and CO<sub>2</sub>, while HNO<sub>3</sub> is reduced either to NO or NO<sub>2</sub> at atmospheric temperatures. Ozone can get destroyed by reacting with trace metals such as iron and manganese. Oxidation of organic material by ozone can also lead to ozone destruction<sup>5</sup>. These reactions are important because they make the surface of soot particles more polar, which increase the efficiency of these particles to act as cloud condensation nuclei.

It has been reported that the precipitation efficiency of the clouds significantly depends on the aerosol loading, especially the CCN. The large concentrations of CCN in the smoke from biomass burning may nucleate many smaller cloud drops<sup>3</sup>. Model simulations show that an increase in carbonaceous aerosol amount can suppress precipitation from low clouds. The large heating of the lower atmosphere due to absorbing carbonaceous aerosols will have a significant influence on atmospheric stability and cloud formation in the tropics, and hence can lead to a weaker hydrological cycle. The aerosol impact on climate can also get enhanced by feedback loops. The atmosphere gets cleansed by scavenging of aerosols during wet precipitation events. The suppression of precipitation by aerosols will prolong their atmospheric lifetimes, thereby enhancing further their impacts. The drier conditions due to the suppressed rainfall in turn are conducive for raising more dust and smoke<sup>3</sup>.



**Figure 1.** Transmission electron microscope image of black carbon aerosol.

Several international programmes, related to aerosol characterization experiment (ACE), are primarily focusing on providing a set of critical measurements to characterize the micro-physical evaluation of aerosols and their impacts. Most recently, the Trans-Atlantic Aerosol & Ocean Science Expeditions (AEROCE) are a series of intensive field experiments being conducted during the Northern Hemisphere spring (March 2006) and summer (June–July 2007) and proposed follow-on cruises in alternating seasons through 2010. More recently, comprehensive measurements of the abundances of carbonaceous aerosols using EC–OC analyser based on Thermal/Optical Transmittance (TOT) method have been conducted during the ISRO-GBP Land Campaigns I (February–March 2004) and II (December 2004) and oceanic regions during the Integrated Campaign for Aerosols, Gases and Radiation Budget (March–May 2006). During wintertime, concentrations of EC (BC) and OC over an urban atmosphere in Northern India typically ranges from 2 to 10  $\mu\text{g m}^{-3}$  and 15 to 120  $\mu\text{g m}^{-3}$  respectively; whereas OC/EC ratios vary from about 5–20 (average: 8.5)<sup>10</sup>. The atmospheric EC concentration measured over Ahmedabad is found to be less than 1  $\mu\text{g m}^{-3}$  during the southwest monsoon, while its abundance is as high as 5  $\mu\text{g m}^{-3}$  in the winter months (with OC/EC ratios: 5–7). The typical concentrations of carbonaceous species and OC/EC ratios measured at



**Figure 2.** Average concentrations of OC and EC along with OC/EC mass ratios in urban aerosols from South Asian region. Dashed line shows the typical urban aerosol OC/EC ratio of ~2.

selected urban sites are presented in Figure 2.

The OC/EC ratios in the Indian urban atmosphere, compared to those reported for the urban sites in the US and Europe are higher. OC/EC ratio over urban locations in the US is ~2, while over Europe, it is ~3. The results from Europe correspond to annual mean values of urban sites over which EC and OC measurements were made under the European Monitoring and Evaluation Programme (EMEP)<sup>11</sup>. OC/EC ratios obtained in Mumbai during March 1999 and the Indian Ocean Experiment (INDOEX) during January–March 1999 were in the range of 1.5–2 (Figure 2). These results correspond to winter, and over an urban, densely populated location and an oceanic region downwind of continental outflow. The higher OC/EC ratios over many locations in India imply the necessity of a re-assessment of model-based aerosol radiative forcing due to elemental carbon over the South Asian region. The aerosol models developed on the basis of micro-physical processes of formation and removal of different aerosol species need to be evaluated with full range of observations, including chemical, physical and optical measurements. Long-term continuous measurements are particularly required to evaluate seasonal variations in atmospheric loading of carbonaceous aerosols and their radiative effects. Radiation absorption is found to depend on the emission source. The absorption by EC is found to increase at least by a factor of 1.5 when coated with reflecting com-

pounds like OC<sup>12</sup>. The hygroscopic growth of carbonaceous aerosols depends on the emission category, for example, diesel soot is strongly hydrophobic while particles produced from forest burning are moderately hygroscopic<sup>12</sup>. The major sources of EC and OC are documented as industrial and vehicular emissions, biomass and fossil fuel burning, however, over a particular region specific sources might contribute to their abundance.

Satellite observations of aerosols are playing an increasingly important role. There is a large variety of instruments and algorithms used for aerosol remote sensing. The new instruments, more specifically designed for aerosol retrievals, such as Polarization and Directionality of Earth's Reflectance (POLDER), Multi-angle Imaging Spectroradiometer (MISR) and Moderate Resolution Imaging Spectroradiometer (MODIS), now provide better measurements of aerosol optical depth with some information on their size distribution. The aerosol sources over India vary from natural (mineral dust and sea salt) to anthropogenic (industrial, vehicular and urban emissions). Coal, petrol and diesel oil are the major fossil fuels used in India for electric power generation, road transportation and in a variety of industries. It should be noted that EC warms the atmosphere while OC cools and their radiative effects depend on the emission source. As the radiative properties of OC and EC depend on the emission sources, not only their absolute concentrations but also their ratios are important in the estimation

of the climate effects. Higher OC/EC ratios over urban sites suggest that comprehensive studies of OC and EC should be carried out in varied locations influenced by different sources over India. Thus, studies need to be designed to assess the regional climate effects of the Indian subcontinent using the optical, physical and chemical characteristics of aerosols obtained from satellite and ground-based measurements taking into account the differences in the scale length of aerosol processes.

1. Solomon, S. *et al.* (eds), In *Climate Change 2007: The Physical Science Basis*. Contribution of Working Group I to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change, Cambridge University Press, Cambridge, UK and New York, NY, USA, 2007, pp. 1–18.
2. Charlson, R. J., Schwartz, S. E., Hales, J. M., Cess, R. D., Coakley, J. A., Hansen, J. E. and Hofmann, D. J., *Science*, 1992, **255**, 423–430.
3. Ramanathan, V., Crutzen, P. J., Kiehl, J. T. and Rosenfeld, D., *Science*, 2001, **294**, 2119–2124.
4. Ramachandran, S., Rengarajan, R., Jayaraman, A., Sarin, M. M. and Das, S. K., *J. Geophys. Res.*, 2006, **111**, doi: 10.1029/2006JD007142.
5. Dentener, F. J., Carmichael, G. R., Zhang, Y., Lelieveld, J. and Crutzen, P. J., *J. Geophys. Res.*, 1996, **101**, 22869–22889.
6. Ramanathan, V., Ramana, M. V., Roberts, G., Kim, D., Corrigan, C., Chung, C. and Winker, D., *Nature*, 2007, **448**, 575–578.
7. Thompson, L. G. *et al.*, *Climate Change*, 2003, **59**, 75–99.
8. McConnell, J. R. *et al.*, *Science*, 2007, **317**, 1381–1384.
9. Ammann, M. *et al.*, *Nature*, 1998, **395**, 157–159.
10. Rengarajan, R., Sarin, M. M. and Sudheer, A. K., *J. Geophys. Res.*, 2007, **112**, doi:10.1029/2006JD008150.
11. Yttri, K. E. *et al.*, *Atmos. Phys. Chem.*, 2007, **7**, 5711–5725.
12. Bond, T. C., Habib, G. and Bergstrom, R. W., *J. Geophys. Res.*, 2006, **111**, doi: 10.1029/2006JD007315.

**ACKNOWLEDGEMENTS.** We thank Prof. Chandra Venkataraman, Indian Institute of Technology, Mumbai for providing the TEM image of black carbon aerosol and permitting to use the same in the text.

S. Ramachandran, R. Rengarajan\* and M. M. Sarin are in the Physical Research Laboratory, Ahmedabad 380 009, India.  
\*e-mail: rajan@prl.res.in