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AEROSOL SCAVENGING: MODEL APPLICATION AND SENSITIVITY ANALYSIS IN THE INDIAN CONTEXT

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Abstract. Sulfate aerosols have been found to be the major contributors to precipitation acidity. Thus, in view of the long-term ecological repercussions they have on aquatic ecosystems and their acidity-potential, the present analysis focuses on a case study application of the layer-averaged aerosol-scavenging model (Okita *et al*., 1996) for predicting values of the wet scavenging coefficient and sulfate concentrations in precipitation samples on the basis of the information available for some selected Indian cities. Through sensitivity analysis (Pandey *et al*., 1997) the scavenging coefficient has been found to be very strongly dependent on precipitation intensity. Comparison of model predictions has been done with the measured values for Delhi, Mumbai, Calcutta and Chennai in India.

Keywords: aerosol scavenging, Indian case study, model application

1. Introduction

The combustion of fossil fuels has greatly increased the concentrations of various oxide-forms of nitrogen and sulfur, especially in major cities of India (AQS, 1994), to the point where they have started to adversely affect important biotic components of ecosystems (Odum, 1983). Sulfates have been found to be the major contributors to precipitation acidity specially in the Indian context (AQS, 1994; Ravichandran and Padmanabhamurty, 1994; Khemani *et al*., 1994). They are formed because of the atmospheric oxidation of sulfur dioxide (SO_2) to ammonium sulfate ($(NH_4)_2SO_4$) or sulfuric acid (H_2SO_4). The oxidation of sulfur dioxide produces a variety of secondary acidic sulfate compounds (Cyrys *et al*., 1995; Sirois, 1993), which are products of either homogeneous (gas or aqueous phase) or heterogeneous (gas-particle phase) phase oxidation. In addition, strong acidic aerosols are also emitted (primary acid aerosols) by coal and oil burning power plants and various other industrial activities.

As far as air-borne pollutants (Dignon and Hameed, 1989) are concerned, they are scavenged either near the land-surface by dry deposition or at greater heights by precipitation. In both of these deposition processes, pollutant-release-heights (Sehmel, 1980) and precipitation intensity are quite significant. Most sulfate, nitrate and ammonium compounds, viz. $(NH_4)_2SO_4$, NH_4NO_3 are found to fall within the 0.1–1.0 μm size range. In fact, more significant than dry deposition onto flat

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terrain is the interception of aerosol particles by vegetation stands. The filtering action of forests is so effective that the concentration of particulate sulfate has been found to be about 35% lower in the air underneath the canopy than above it. Rainfall rinses the dry deposited material off the foliage, consequently the rainwater collected below the canopy is enriched with sulfate and other trace particles (Warneck, 1988; Erisman *et al*., 1995).

When we look at the rainfall pattern in the Indian sub-continent, there are two monsoons. The southwest, or summer monsoon, with warm winds blowing from the ocean over almost the entire country causes copious amounts of rainfall between June and September. The northeast or winter monsoon is characterized by a dry continental airmass blowing from the vast Siberian high-pressure area from December to March. Except for the coastal strip in the southeastern portion of South India and in the extreme northern portion over Kashmir, the rest of the country during this season receives practically no rainfall. Heavy rainfall is confined largely to the southwestern, eastern, and the northeastern portions of the country. The central region and the Gangetic plain lie in the zone of moderate rainfall, while the north Deccan and adjoining areas receive heavy rainfall towards the end of the monsoon season. The eastern districts of Andhra Pradesh and Tamil Nadu receive most of their rainfall from October to December due to severe cyclonic storms that form in the central and the southern Bay of Bengal and move west or north-east across the peninsula (Bobba *et al*., 1997).

In the present article, which is based on Indian precipitation-intensity data (Bobba *et al*., 1997) a layer-averaged model (Okita *et al*., 1996) has been applied for predicting values of the wet scavenging coefficient for sulfate aerosols. Subsequently, sulfate concentration in precipitation samples has been predicted through its dependency on sulfate aerosol concentrations in air (AQS, 1994), mixing heights (Maske *et al*., 1982) and precipitation intensities (Bobba *et al*., 1997) for these cities. The strong dependence of the scavenging coefficient on precipitation intensity has been established through sensitivity analysis (Pandey *et al*., 1997). Model predictions have been compared with measured values for the four major Indian cities: Delhi, Mumbai, Calcutta and Chennai shown in Figure 1.

2. Sulfate Aerosols and Atmospheric Ammonia: Interactions and Impacts

Already there is strong evidence to show that aerosols lead to respiratory diseases, chronic bronchitis being one of their most frequently encountered health impacts (Spengler *et al*., 1990). Sulfate aerosols are mainly formed through processes such as nucleation or condensation, adsorption of secondary pollutants and oxidation of primary SO_2 absorbed in aqueous aerosols (liquid-phase oxidation). Strong acidic aerosols are also emitted from coal-based power plants and various other similar industrial activities using coal and oil. Continuously rising concentrations of sulfur compounds in the atmosphere is attributed to the combustion of fossil fuels, mainly

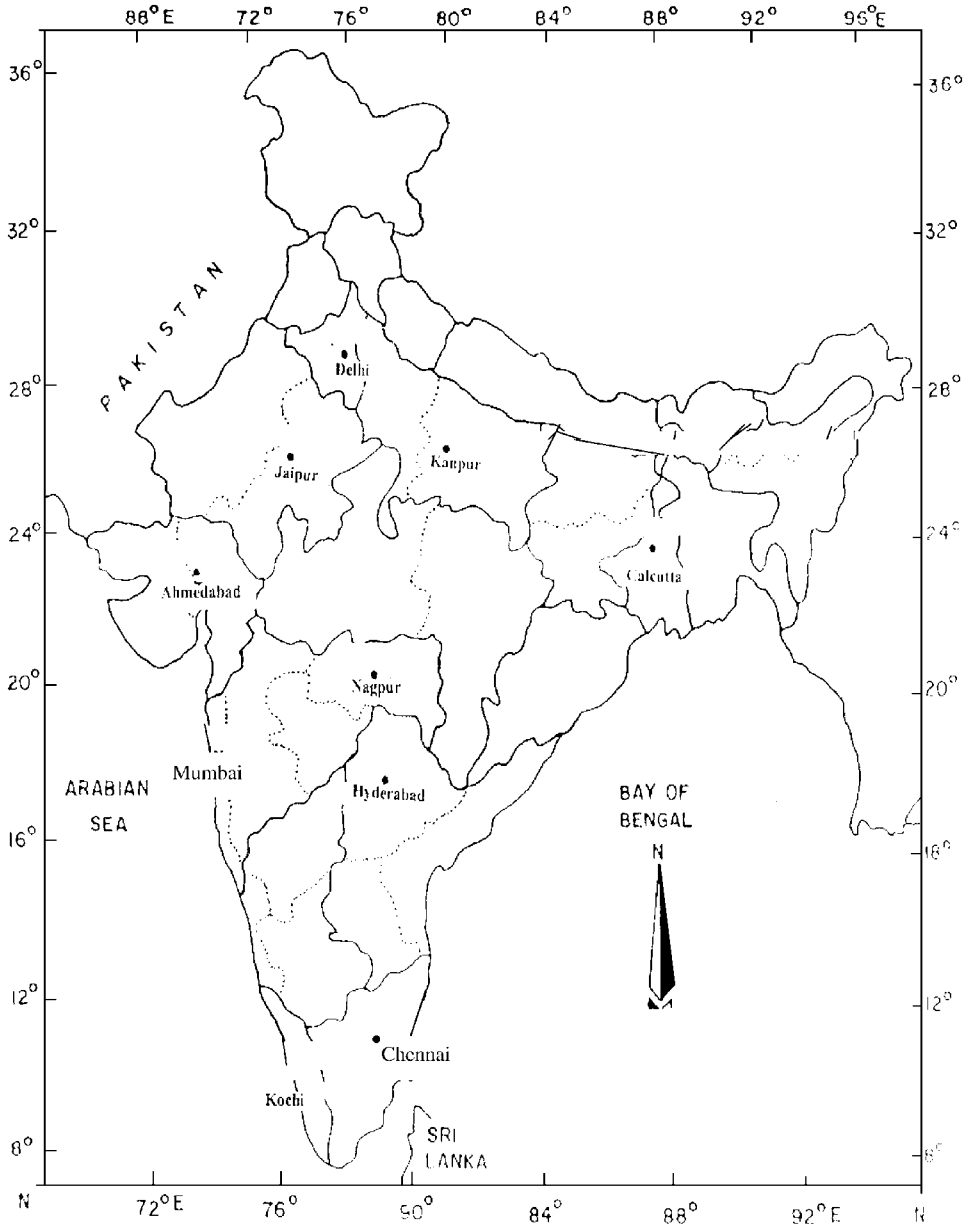

Figure 1. Map of India.

coal (Singer *et al.*, 1996). A significant fraction of sulfur emitted into the atmosphere either as a primary aerosol or as the product of gas-to-particle conversion ends up as a quite stable submicron aerosol (Whitby, 1977). Thus, importance of sulfur as a major component of particulate matter in the atmosphere is well known. What is, however, less well known is the amount of acidity associated with the sulfate (SO_4^{2-}) particles (Brook *et al.*, 1997).

As far as ammonia-emission is concerned, combustion, bacterial decomposition of animal excreta, and emanation from soils are its main sources. Reported NH_3-emission factors are: 1 g kg^{-1} for coal, 0.12 kg m^{-3} for fuel oil, 10 mg m^{-3} for natural gas, 1.2 g kg^{-1} for wood and 0.15 g kg^{-1} for forest fires. Present mainly as organic nitrogen, the nitrogen content of coal is 1–2% by mass, of which a large fraction is released as NH_3 upon heating (Warneck, 1988; Erisman *et al.*, 1995).

Acidic sulfate aerosols are formed through both gaseous and aqueous phase oxidation of SO_2. These aerosols, after rapidly reacting with gaseous ammonia (NH_3), produce various molecular forms of SO_4^{2-}, viz. NH_4HSO_4 and $(NH_4)_2SO_4$. And consequently, spatial and temporal predictions of sulfate aerosols are beset with a large number of uncertainties. For instance, there is a large spatial heterogeneity in the spatial distribution of NH_3-sources, and in ambient NH_3-concentrations. Then, there are issues concerning the transportation of aerosols (Cyrys *et al.*, 1995), their travel distances and durations (Figure 2). These issues combined with uncertainties associated with spatial distributions (both vertically as well as horizontally) of ammonia-based aerosols become still more complicated (Lipfert *et al.*, 1993; Brook *et al.*, 1997). The behavior of hygroscopic aerosols in cloud and rain is complicated by the variation in size that occurs with changing relative humidity. Most of the sulfate aerosols at cloud forming altitudes are usually in the range of 0.02–0.5 μm radius. At saturation these particles may form droplets of the size of 0.2–10 μm radius.

In fact, the exchange of atmospheric ammonia amongst various surfaces may be bi-directional depending on the types of surfaces involved and ambient environmental conditions. While grazed pastures and arable cropland result in net ammonia emissions, forest ecosystems (Pandey *et al.*, 1995) serve as net ammonia depositors (Warneck, 1988; Erisman *et al.*, 1995). Ammonia is also taken up, translocated and metabolized by living plants. Deposition of NH_3 to vegetated surfaces can take place either by stomatal uptake (Pandey *et al.*, 1998) or by several external and internal plant parts.

3. Scavenging of Aerosols: Model Application and Sensitivity Analysis

Airborne pollutants are scavenged in the surface layer by dry deposition and at greater heights by precipitation. In both of these deposition processes, pollutant-release-heights and precipitation intensity are quite significant (Sehmel, 1980). While dry deposition includes removal of pollutants due to impaction with ve-

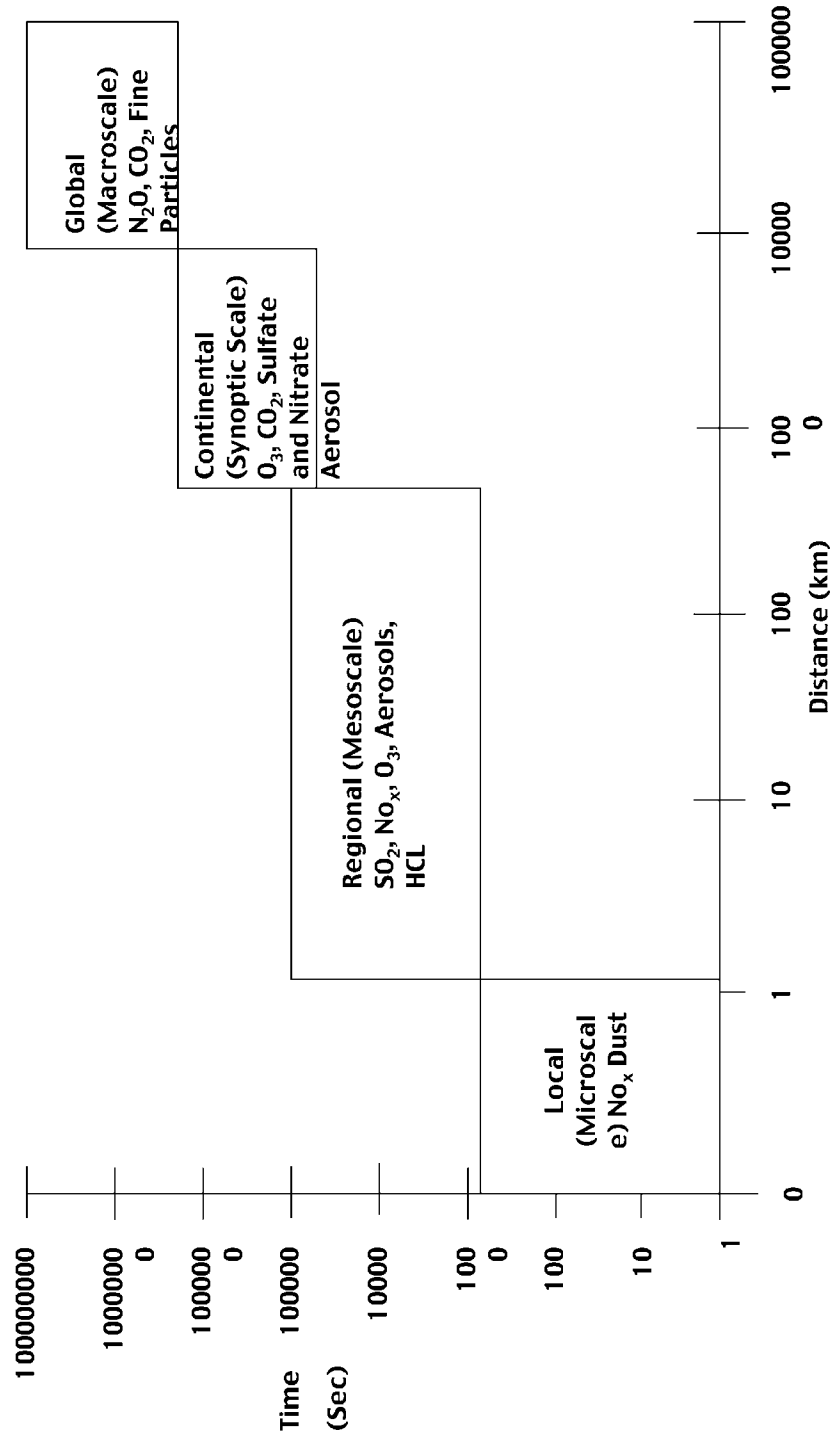

Figure 2. Temporal and spatial distribution of atmospheric pollutants (Cyrys *et al.*, 1995).

TABLE I
Input values

S. No.	City	Precipitation intensity (mm hr^{-1})	Sulfate in air ($\mu g\ m^{-3}$)	Mixing height (km)
1.	Delhi	0.0684	10.20	1.60
2.	Calcutta	0.3420	13.40	1.20
3.	Mumbai	0.2268	12.40	0.80
4.	Chennai	0.1116	7.50	1.60

getation etc. near the surface or due to chemical reactions, wet scavenging includes processes such as the attachment of gaseous and aerosol pollutants to cloud droplets (rainout), ice crystals and rain drops (washout) followed by droplet removal from the atmosphere to the earth's surface by rain or snow (Boubel *et al.*, 1994; Samara and Tsitouridou, 2000). Deposition processes limit aerosols' lifetime in the atmosphere, control the distances travelled before deposition, and thus affect their atmospheric concentrations. The deposition velocity, however, depends, inter alia, on particle size also. Dry deposition is capable of filtering the larger particles from the atmosphere in 2 to 3 days, and would require several weeks to remove the more harmful submicron-fraction, which is, however, removed through various wet deposition processes. That is why understanding of wet deposition processes assumes immense significance from the human health and ecosystem-health point of view.

Changes in air concentration caused by wet deposition are often represented by an exponential decay process (Okita *et al.*, 1996). The rate of change in aerosol-concentration (A_{ero}) in the air is given by:

$$\frac{d(A_{\text{ero}})}{\mathrm{d}t} = -W_s(A_{\text{ero}}) \ , \tag{1}$$

where W_s is the wet scavenging coefficient (s^{-1}), and is dependent, inter alia, on particle size and rainfall intensity (Meyers, 1998; Slinn, 1977). It has also been represented as a function of the following form (Okita *et al.*, 1996):

$$W_s = a(P)^b \ , \tag{2}$$

where P is the rainfall rate (mm hr^{-1}), and values for parameters 'a' and 'b' are given in Okita *et al.* (1996).

As the scavenging coefficient is dependent on the precipitation intensity, it has been computed based on the information available in Bobba *et al.* (1997) for these cities, wherein annual precipitation intensity values for all these cities are given.

The annual precipitation values given for Delhi, Mumbai, Calcutta and Chennai are respectively 60, 300, 200 and 100 cm. Based on these figures precipitation intensities have been computed in mm hr^{-1} and shown in Table I. While referring to Bobba *et al*. (1997), one pertinent fact, which needs to be especially stated is that Mumbai and Chennai are the new names given to the cities of Bombay and Madras as has been cited by Bobba *et al*. (1997) in their Figure 6 (p. 371). The values of parameters 'a' and 'b' in Equation (2) were taken from Okita *et al*. (1996). Values of sulfate aerosols for Indian cities were taken from AQS (1994). Information on mixing heights was taken from Maske *et al*. (1982). Subsequently, the following expression was used for estimating aerosol-concentration in precipitation (Okita *et al*., 1996):

$$(A_{\text{ero}})_{pw} = 10^{-6}(A_{\text{ero}})_{\text{air}}(W_s)\left(\frac{H}{P}\right) , \tag{3a}$$

where $(A_{\text{ero}})_{pw}$ is the aerosol-concentration (mg L^{-1}) in precipitation; $(A_{\text{ero}})_{\text{air}}$ is the aerosol concentration (μg m^{-3}) in air; P is the precipitation intensity (cm^{-1}) and H the mixing height (cm). When P is expressed in 'mm hr^{-1}' and H in 'km', Equation (3a), because of additional conversion factors, assumes the following form:

$$(A_{\text{ero}})_{pw} = 3600.0(A_{\text{ero}})_{\text{air}}(W_s)\left(\frac{H}{P}\right) . \tag{3b}$$

The expressions required for sensitivity analysis have been derived in the form (y_x), where x is the independent variable with respect to which sensitivity is being studied, and y is the dependent variable, in which the consequent changes need to be analyzed (Pandey *et al*., 1997). The derived sensitivity expressions with respect to a (W_{s_a}), b (W_{s_b}) and precipitation intensity P (W_{s_P}) are given below:

$$W_{s\_a} = (P)^b , \tag{4}$$

$$W_{s\_b} = k\ln(P) , \tag{5}$$

$$W_{s\_P} = a(P)^{b-1} . \tag{6}$$

4. Results and Discussion

The input values used in this exercise have been shown in Table I. For sulfate in air (μg m^{-3}) the values for summer season, which just precedes the rainy season have been taken from Air Quality Status Report (AQS, 1994). Values for rainy season (in air) have not been used, as they would depict the resultant of the actual air-concentration minus the scavenged concentration. The scavenging coefficient has

thereafter been computed on the basis of Equation (2) with the model parameter values of a and b taken from Okita *et al*. (1996). Then, sulfate concentration in rain-water $[(A_{\text{ero}})_{pw}]$ was computed through a computer program based on Equation (3) and written in 'Turbo-C'. This program also computed the values of different sensitivity expressions (Equations (4) through (6)). The input values alongwith the computed values for scavenging coefficient have been shown in Figures 3a and b. Model predicted values have been compared with their measured values in Figure 4a. Figure 4b then plots the results of sensitivity analysis.

Scavenging coefficient for Calcutta is found to be the maximum (6.2×10^{-5}) and for Delhi the minimum (1.9×10^{-5}) (Figure 3b). This is due to their significantly different rain-fall patterns. As far as Calcutta and Chennai are concerned the measured concentrations of sulfate in rain-water (AQS, 1994) happen to be very close to the model predictions (Figure 4a). However, for Delhi and Mumbai, the differences are quite large. Therefore, the role of dry deposition and its spatial distribution calls for closer look.

As far as wet deposition is concerned, it is normally very evenly distributed over large surface areas, except in upland areas where rainfall intensity is quite high. Dry deposition, however, varies substantially at local and regional scales depending on the aerodynamic roughness, collecting efficiency and forest density in different locations. Gases and aerosols can be deposited on needles/leaves, branches and trunks. The collecting efficiency of these canopy elements depends on their size and shape. Small 'needle-like' structures have been reported to be more effective in filtering gases and aerosols (Draaijers *et al*., 1992). Delhi is very close to hilly areas on its north and it is quite likely that various forest zones in these uphill areas have intercepted significant amount of aerosols in terms of dry deposition. And this may be the main reason why its actually measured value has been found to be much lower than the model predicted value. Mumbai is on the sea-coast, sea being on the west, and it is a highly industrialized city with scanty vegetation on the other side. And, it is most likely that this lack of effective vegetation-filter contributed towards the significantly higher aerosol-concentration measured in Mumbai-rain-water. As far as sensitivity analysis is concerned, a very strong dependence of aerosol-scavenging on precipitation intensity (P) is observed (Figure 4b). The graphs have been plotted in such a way as to get the best resolution possible. For example, to get the actual value for W_{s_b}, the values shown in Figure 4b (for W_{s_b}) are to be multiplied by a factor of 10^{-5}. The values of W_{s_a} and W_{s_P}, however, remain the same in the order of magnitude.

5. Conclusion

In India, a nation-wide air-quality monitoring network started in 1978. The programme sponsored by the Central Pollution Control Board has generated a time-series on air quality of ten major cities including Delhi, Mumbai, Calcutta and

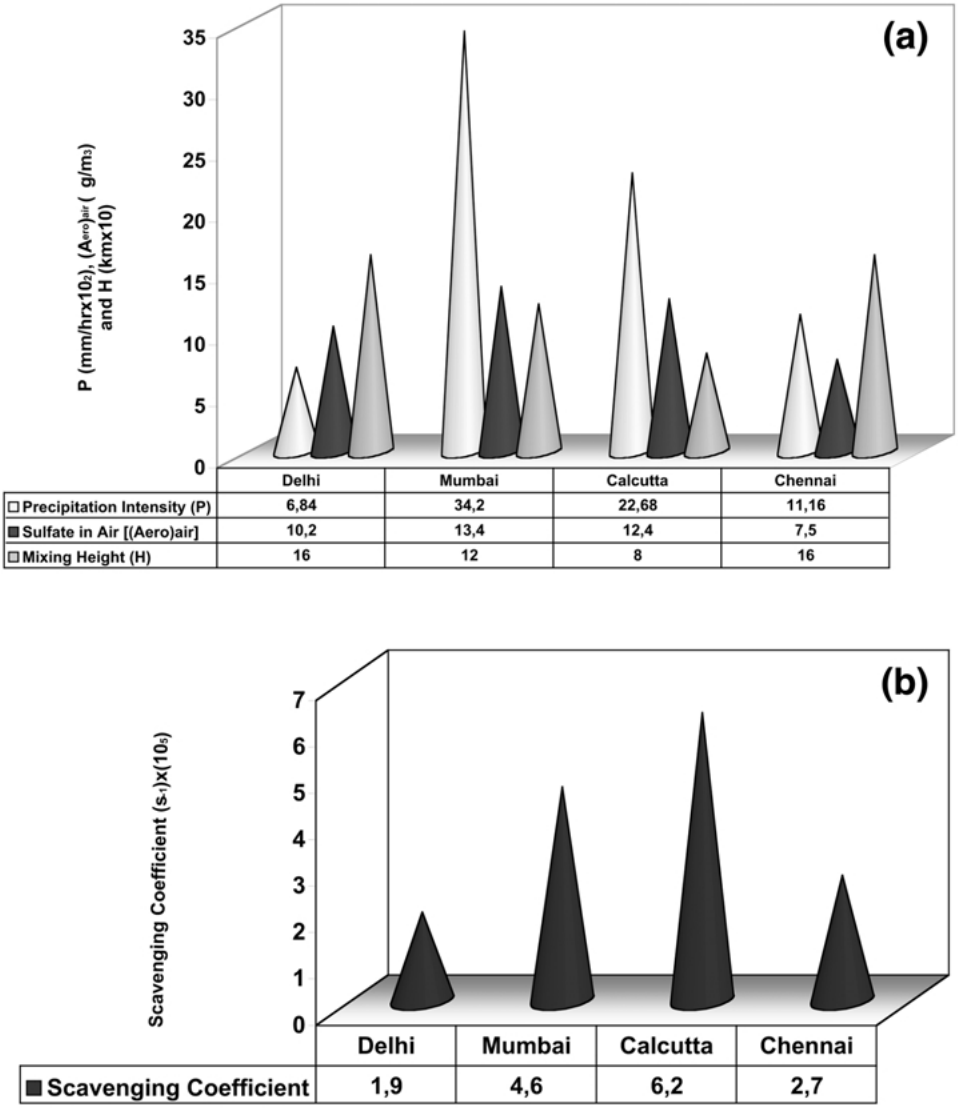

Figure 3. (a) Input Values ($(A_{\text{ero}})_{\text{air}}$: Sulfate in Air ($\mu$g m^{-3}), P: precipitation intensity (mm hr^{-1}) $\times$ 2 and H: mixing height (km) $\times$ 10). (b) Scavenging coefficient (s^{-1}) $\times$ 10^5 (normalized values).

Chennai (NEERI, 1997). The present article focuses on predicting the sulfate concentration in precipitation samples by applying a layer-averaged model (Okita *et al.*, 1996), which initially estimates the values of wet scavenging coefficient on the basis of precipitation data available for four Indian cities: Delhi, Mumbai, Calcutta and Chennai. These city-wise estimates for scavenging coefficients have thereafter been used for predicting the sulfate concentration in rain-water. The model, inter

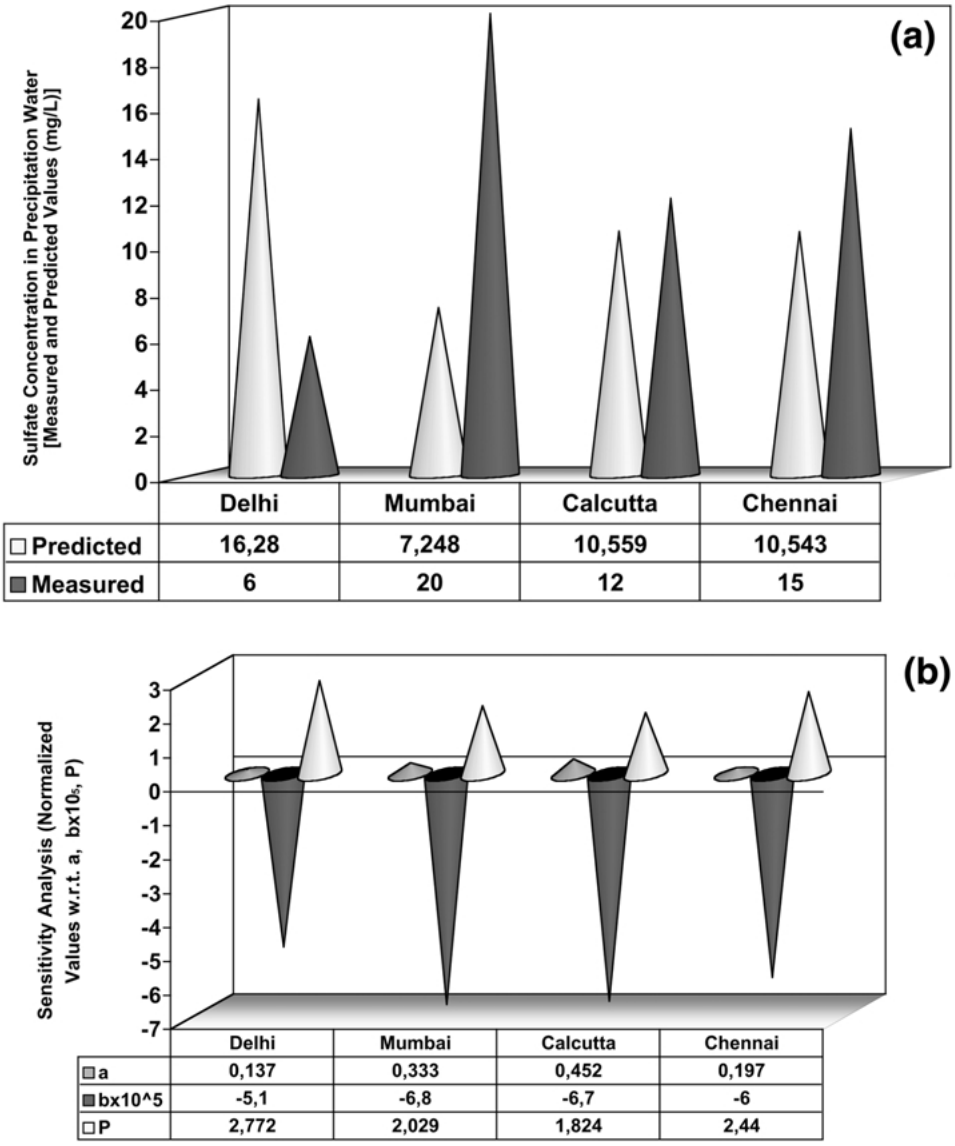

Figure 4. (a) Model validation; (b) sensitivity analysis.

alia, is dependent on sulfate aerosol concentration in air (AQS, 1994), mixing heights (Maske *et al*., 1982) and precipitation intensities (Bobba *et al*., 1997) for these cities. Sensitivity analysis explores the linkages of aerosol scavenging coefficient with the related parameters and finds that it (scavenging coefficient) has maximum dependence on the precipitation intensity.

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