

Variations in the concentrations of ionic species in rain events at Pune

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In the present work, evolutions of the concentrations of major neutralizing agents (Ca^{2+} and NH_4^+) and acidic species (SO_4^{2-} and NO_3^-) are computed with Slinn's model using the initial number concentrations of particle size distributions measured at Pune during 1998-1999. Theoretically predicted ionic concentrations are compared with observed ionic concentrations in the sequential samples collected in the rain events at Pune. Also, equivalent ratios $[(\text{SO}_4^{2-} + \text{NO}_3^-)/(\text{Ca}^{2+} + \text{NH}_4^+)]$ are computed theoretically to study the neutralizing capacity of the atmosphere during precipitation events and compared them with observed ones. The variation of observed equivalent ratios with accumulated rain (mm) indicated that acidic components are always neutralized with neutralizing species.

Keywords: Ionic species, Rain events, Ionic concentration, Particle size distributions

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1 Introduction

The rainwater concentration at the ground is the quantity measured in rainwater-chemistry field experiments. Most of the rainwater-chemistry field data including sequential wet deposition have not been supplemented by aerosol mass size distribution and their chemical composition before and after rain, rain-drop size spectra and humidity profiles during rain. The field measurements of the below-cloud scavenging of atmospheric particulate concentrations during precipitation obtained apparent washout coefficients by knowing just the particle size distribution before and after a fall of rain and duration of rain¹. However, raindrops falling through the cloud of the atmospheric aerosol constituted by admixtures of various metals, salt particles and other chemical compounds collect the aerosol particles present in their path^{2,3}. Ionic concentration in rainwater samples collected sequentially during a single precipitation event varies with respect to the removal rate of aerosol particulate suspended in the atmosphere by wet scavenging processes. Wet scavenging process classified as the cloud scavenging responsible for removal of particulate compounds by raindrops below the cloud base. The aim of this work is to study the aerosol scavenging potential and its role in the composition of the precipitation with the help of sequential samples collected during the rain events of 1990, 2001 and 2002. The study deals with

the theoretical prediction of the evolution of the concentrations of acidic species (SO_4^{2-} and NO_3^-) and of major neutralizing agents (Ca^{2+} and NH_4^+) during rain events of heavy rain regime and compares the results with the observed evolution of the concentration of these species.

The equivalent ratios $(\text{SO}_4^{2-} + \text{NO}_3^-)/(\text{Ca}^{2+} + \text{NH}_4^+)$ were calculated at 1-mm intervals of accumulated rain for the precipitation events considered to study the neutralizing capacity of the atmosphere in the final stages of precipitation events, when major neutralizing agents have been scavenged. Theoretically predicted equivalent ratios were compared with the equivalent ratios based on observed data.

2 Theory

The scavenging coefficient $\lambda(D_p, t)$ is defined as removal rate of the aerosol number concentration $N(D_p)$ with the following expression,

$$dN(D_p)/dt = -\lambda(D_p, t) N(D_p, t) \quad \dots (1)$$

with

$$\lambda(D_p, t) = \int_0^\infty (\pi/4) D^2 E(D_p, D) V_t(D) N(D) dD \quad \dots (2)$$

where $E(D_p, D)$ is a collision efficiency of the rain-drop of diameter D for the aerosol particle of diameter D_p , $V_t(D)$ the terminal velocities of raindrops and N

(D) the lognormal distribution of raindrops with rain intensity of 25 mm h^{-1} as reported by Seinfeld⁴. Integrating Eq. (1), number concentration of aerosol particles $N(D_p, t)$ at time t during scavenging event is given as,

$$N(D_p, t) = N(D_p, 0) \exp[-\lambda(D_p, t)] \quad \dots (3)$$

where $N(D_p, 0)$ is the initial number concentration. Collision efficiency $E(D_p, D)$ is obtained by considering the three important scavenging mechanisms such as Brownian diffusion, inertial impaction and interception using Slinn's model⁵. Terminal velocities $V_t(D)$ are computed from Beard's formulae⁶. Assuming a lognormal distribution for the $N(D)$ with heavy rain intensity (25 mm h^{-1}), the precipitation scavenging rates are computed for different size particles using Eq. (2). The ionic concentration depends not only on the mass of aerosol scavenged, but also on the volume of rainwater in which the mass accumulated. For a rainfall rate of R (in mm h^{-1}), Pruppacher and Klett⁷ give the mass of water (W_L), in a cubic metre of air, as

$$W_L (\text{g m}^{-3}) = R \rho_w / 3.6 V_t(D) \quad \dots (4)$$

where ρ_w is the density of water in g m^{-3} and $V_t(D)$ the terminal velocity in m s^{-1} .

Evolutions of particle size distributions are obtained from their measurements (initial number concentration) at Pune during premonsoon months^{8,9} of 1998-1999, using Eq. (3), and the rainwater concentrations are computed with Eq. (4). Theoretical results are compared with the observed rainwater concentrations of rain events.

3 Results and discussion

It is an established trend that ionic concentration varies during single precipitation event. Results obtained by different researchers on sequential sampling of rain showed a decrease in ionic concentrations during initial stages of a rainfall event¹⁰⁻¹². In the present study, theoretically computed concentration of Ca^{2+} , SO_4^{2-} , NH_4^+ , NO_3^- in rainwater shows an exponential decrease throughout a precipitation event (25 mm h^{-1}) with a sharper decrease in ionic concentration at the beginning of the event as evident from Fig. 1. The higher ionic concentrations of Ca^{2+} , SO_4^{2-} , NH_4^+ , NO_3^- in the initial amount of accumulated rain may be due to rapid below-cloud scavenging of components that are of local origin (Fig. 1). Predicted rainwater ionic concentration as a function of accumulated rain shows a similar trend as observed by different investigators¹⁰⁻¹².

Figure 2 shows the evolution of SO_4^{2-} and Ca^{2+} deposition for the precipitation events considered with accumulated rain of 1 mm interval. Theoretical curves for the evolution of SO_4^{2-} and Ca^{2+} deposition are also shown. Observed deposition of SO_4^{2-} is slightly higher for rain event of 19 Sep. 2001 and Ca^{2+} is higher for rain event of 27 June 2001. Neutralizing species (Ca^{2+}) might have depleted due to below-

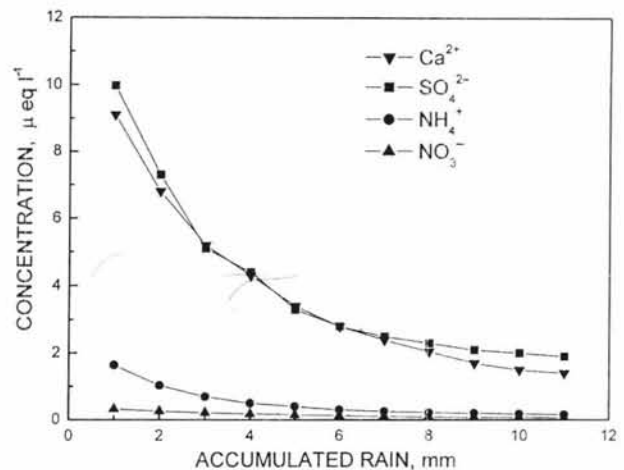


Fig. 1—Theoretically predicted variation of ionic concentrations of major neutralizing and acidic components as a function of accumulated rain (mm)

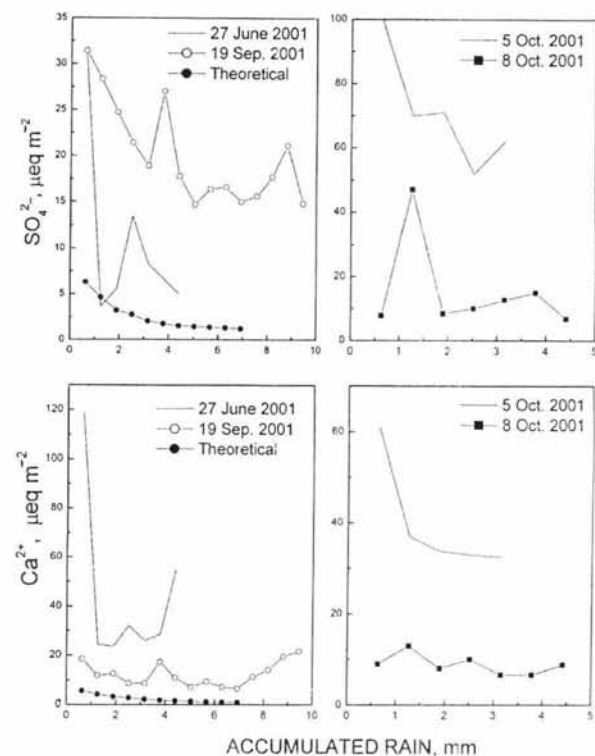


Fig. 2—Evolutions of deposition of SO_4^{2-} and Ca^{2+} as a function of accumulated rain

cloud scavenging during monsoon (September) resulting in relatively more deposition of SO_4^{2-} in the rain event of 19 Sep. 2001. Rain event of 5 October shows higher deposition of Ca^{2+} and SO_4^{2-} in comparison to that of 8 Oct. 2001. Theoretically predicted deposition of Ca^{2+} and SO_4^{2-} varies with rain amount and follows an inverse relationship. Theoretical deposition levels for Ca^{2+} and SO_4^{2-} are much lower as compared to those of observed ones.

In Fig. 3 the observed rain events recorded in the year 2001 for the ionic concentrations of Ca^{2+} , SO_4^{2-} , NH_4^+ and NO_3^- in rain water samples collected sequentially on 27 June (onset of monsoon), 19 September (during monsoon) and 8 October (post-monsoon) are shown. The rain events on 27 June and 19 September show a well-known trend of ionic concentration observed by different researchers for the case of sequential sampling of rain. There exists an inverse relationship between accumulated rain amount (mm) and ionic concentration during the initial stages of rainfall events of 27 June and 19 Sep. 2001. Further, it is noted that in the rain event of 27 June, the concentration of Ca^{2+} is highest as compared to SO_4^{2-} , NH_4^+ and NO_3^- , whereas in the rain event of 19 Sep-

tember, the concentration of NH_4^+ is slightly higher as compared to Ca^{2+} , SO_4^{2-} , and NO_3^- . The higher concentration of Ca^{2+} in the rain event of 27 June may be due to below-cloud scavenging of particles mainly of local continental origin during the onset of monsoon. Slightly higher concentration of the NH_4^+ in the rain event of 19 September may be due to below-cloud scavenging of particles of fertilizers that were used in the agricultural land few kilometres away from this location during later stages of monsoon. As the major ionic components are washed out from the atmosphere during monsoon season (June - September) the ionic concentrations of Ca^{2+} , SO_4^{2-} , NH_4^+ and NO_3^- are comparatively less in the rain event of 8 Oct. 2001. This rain event does not show any specific trend and needs further observational study during winter.

The equivalent ratios of acidic species ($\text{SO}_4^{2-} + \text{NO}_3^-$) to neutralizing agents ($\text{Ca}^{2+} + \text{NH}_4^+$) were calculated at 1 mm interval of rain amount for the observed precipitation events. Equivalent ratios as a function of rain amount are plotted in Fig. 4. Equivalent ratios vary with accumulated rain and its value 1 indicates that acidic species were always neutralized

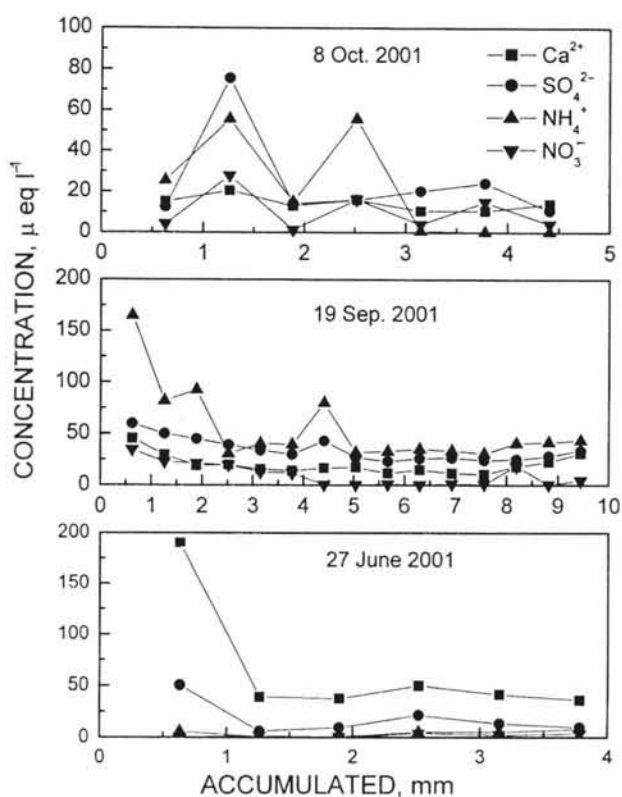


Fig. 3—Evolution of ionic concentrations of Ca^{2+} , SO_4^{2-} , NH_4^+ and NO_3^- with accumulated amount of rain (mm)

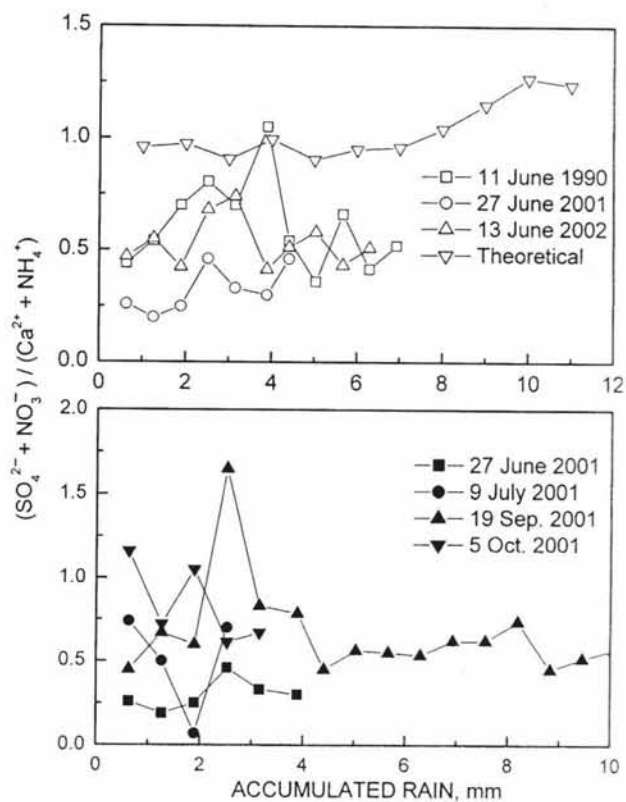


Fig. 4—Variation of equivalent ratios $[(\text{SO}_4^{2-} + \text{NO}_3^-) / (\text{Ca}^{2+} + \text{NH}_4^+)]$ as a function of accumulated rain (mm)

due to the particles in the admixtures of calcium compound present in the atmosphere as a result of the wind-blown dust during premonsoon months. Occasionally, equivalent ratios are found slightly greater than one in the observed rain event. Theoretical equivalent ratios based on observed particle size distributions at Pune^{8,9} are also plotted for comparison in Fig. 4. Theoretically predicted equivalent ratios greater than one at the later stages of rain event (accumulated rain > 8 mm) imply that concentration of calcium compounds depleted due to below-cloud scavenging in the initial stages of precipitation events. In this case, other neutralizing species (NH_4^+) might have accounted for the neutralization of acidic species. The discrepancy between the theoretical calculations and observed results may be due to the use of the available data of particle size distributions of different years for comparison. However, the factors such as polydispersity of the aerosols, scavenging due to electrical and thermophoresis effect, etc. are also responsible, to some extent, for the deviation of observed values from theoretical one. The present results are expected to give better understanding of the scavenging of acidic aerosols by precipitation in the acid rain problem in India. Some of the rainwater samples collected at Delhi¹³ showed acidic nature due to the presence of sulphuric and nitric acid.

4 Summary and conclusion

Theoretically predicted ionic concentration for assumed precipitation event (25 mm h^{-1}) exponentially decreases with accumulated rain and is in agreement with an established trend observed in earlier studies¹⁰⁻¹².

Evolutions of SO_4^{2-} and Ca^{2+} deposition for the precipitation events considered in this study have shown variation in their deposition levels in accordance with period when the sequential samples were collected. For example, higher concentration of Ca^{2+} in the month of June and slightly higher concentration of SO_4^{2-} in the month of September 2001 are observed.

Ionic concentrations of Ca^{2+} , SO_4^{2-} , NH_4^+ and NO_3^- as a function of accumulated rain (mm) have shown seasonal variation. The Ca^{2+} concentration is higher during onset of monsoon and NH_4^+ is slightly more during monsoon. Both neutralizing agent (Ca^{2+} and NH_4^+) and acidic species (SO_4^{2-} and NO_3^-) were washed out during monsoon (June-September) and

resulted in relatively less ionic concentrations in the sequential samples of October (postmonsoon).

Observed equivalent ratios of acidic species ($\text{SO}_4^{2-} + \text{NO}_3^-$) to neutralizing agents ($\text{Ca}^{2+} + \text{NH}_4^+$) were found to be less than one throughout the rain events. Therefore, acidic species are always neutralized by neutralizing agents. However, predicted equivalent ratios go beyond one after 8 mm of accumulated rain, indicating the depletion of Ca^{2+} from the atmosphere due to below-cloud scavenging of heavier particles of admixtures of calcium compounds.

Observed ionic concentrations of Ca^{2+} , SO_4^{2-} , NH_4^+ and NO_3^- and magnitudes of their deposition level are much higher than the theoretical ones. Inclusion of polydispersity of the aerosols in the computations of scavenging rates may further improve the theoretical results.

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