

# Variation in the ionic composition in convective showers in Pune, India

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## ABSTRACT

Rain water samples of equal volume (100 ml) were collected sequentially from 5 convective shower events for a period of 2 years during the summer monsoon seasons of 1988 and 1989 at Pune. A marked decrease in the concentrations of soil-oriented elements  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  was observed in the first few samples in all the events followed by a decrease in pH of the subsequent samples. Surprisingly,  $\text{SO}_4^{2-}$  also showed similar variation, indicating that soil is contributing some  $\text{SO}_4^{2-}$  in rain water. Washout process appears to be an important mechanism for the removal of the major ions from the atmosphere. However, rainout processes seem to be important for the removal of  $\text{NO}_3^-$  ions. The study points out that sequential sampling during a single shower appears to give better information about the relationship among  $\text{H}^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$  as compared to bulk sampling for longer duration.

## 1. Introduction

Research in precipitation chemistry has intensified in recent years because of increased awareness of the actual and potential ecological and economical problems caused by acid rain (Likens and Borman, 1974; Likens et al., 1979; Rodhe et al., 1988). Most of the data on the chemical composition of precipitation are reported from the samples collected over the period of a month, a week, a day or recently a single event. While the data obtained from studies employing these types of collection procedures are useful in determining the net loading of constituents and understanding the influence of acid material and soil dust on acidification of rain water. However, such samples which are collected over relatively long time spans, do not allow a description of the mechanism by which various chemical constituents enter precipitation, nor do they indicate how changes in meteorological conditions during a single event affect the chemical composition of the precipitation.

For determining the contribution of various atmospheric processes to the overall chemical composition of rain, several authors have pointed out the importance of collecting samples on a short-time scale within a single precipitation event (Baker et al., 1981; Raynor and Hayes, 1981). Relatively few published results on sequential sampling and data analysis have been documented (Gatz and Dingale, 1971; Raynor and McNeil, 1979; Seymour and Stout, 1983).

For understanding the role of individual ionic components on acidification processes, 66 rain water samples of equal volume were collected from the 5 convective showers at Pune ( $18^\circ 32' \text{N}$ ,  $73^\circ 51' \text{E}$  559 m asl) during the southwest monsoon seasons of 1988 and 1989. Also, efforts were made to identify the sources of ionic components and their incorporation in rain water.

## 2. Sampling procedure

Rain water samples of constant volume (100 ml) amounting 0.6 mm rainfall, were collected at Pune on the terrace of Institute's building at a height of

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about 15 m above ground by using a stainless steel funnel of 45 cm diameter fitted on 1 litre capacity polyethelene bottle which was previously rinsed with tripple distilled water. A rain water sample of 100 ml volume was collected and duration of each sample was recorded. The sample was transferred to another polyethelene bottle of 100 ml capacity which was previously rinsed with tripple distilled water. The procedure was repeated for every 100 ml of rain sample until rain ceased. 43 rain water samples from 3 rain events and 23 rain water samples from 2 events were collected in 1988 and 1989 respectively. An event was considered to be convective shower, when the intensity of rainfall was observed  $\geq 10 \text{ mm h}^{-1}$  and lasted for about 40 minutes. The number of samples in an event varied from 10 to 17 and duration of sample collected varied from 0.5 to 9.5 min in the total of 66 samples. The pH and specific conductivity were determined immediately after the collection of samples. Afterwards all the rain water samples were filtered through Whatman 41 filter paper and refrigerated at  $4^\circ\text{C}$  in the laboratory until all the major ionic components were analysed.

### 2.1. Analytical methods

The concentration of  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  were determined by using Perkin-Elmer 373, double beam atomic absorption spectrophotometer with air-acetylene flame. The detection limits for  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  are 0.09, 0.05, 0.125 and  $0.04 \mu\text{moles l}^{-1}$  respectively. The concentrations of  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$  were determined using Uv/visible Spectrophotometer. The  $\text{SO}_4^{2-}$  was determined by barium iodate method (Klockow and Ronicke, 1973). The  $\text{NO}_3^-$  was determined by brucine method (Jenkins and Medsken, 1964). The detection limits for  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$  were 1.0 and  $0.16 \mu\text{moles l}^{-1}$  respectively.

The calibrations for different chemicals constituents were obtained by preparing low-level standard solutions using grade chemicals. These calibrations were periodically repeated to check the accuracy. The analytical errors were nominal and varied within  $\pm 10\%$ .

The pH values were measured with digital pH meter using reference (KCl) and glass electrodes standardized with pH 4.0 and pH 9.2 reference buffers before pH determination. The buffer solutions were prepared by dissolving standard buffer

tablets in 100 ml tripple distilled water. The accuracy of pH meter is  $\pm 0.01$  pH and response time is 30 seconds. Average of three stable pH readings for each sample was reported.  $\text{H}^+$  values were deduced from pH values.

## 3. Results and discussion

### 3.1. Variation in ionic components

The concentrations of ionic components in  $\mu\text{eq l}^{-1}$  along with pH and specific conductivity of rain water collected during the summer monsoon seasons of 1988 and 1989 are given in Table 1. For brevity, data for only 5 of the total samples in each event are shown since they adequately represent the changes that take place.

The pH value in the individual samples varied between 7.23 and 5.87. In 5 of the precipitation events, the pH value decreased by 0.3 to 1.0 unit. The most rapid decrease in pH occurred during the early portion of the rainfall event, while only small decrease was noticed in the pH value during the later portion of the event. The specific conductivity of the rain water decreased progressively except in the event which occurred on 26 July 1988. This could be attributed to the effect of washout of coarse particulate materials which contain various soluble salts. As these materials are removed early in the event, the rain water collected during the later portion of the event is representative of rainout, or those components present in the cloud layer itself. The initial specific conductivity in the samples collected on 26 July 1988 was the lowest as compared to other four events (Table 1). This could be due to the occurrence of an earlier shower, samples of which could not be collected. The shower continued for 2 h and gave 8 mm rainfall which might have washed out the ionic components.

The concentration of  $\text{SO}_4^{2-}$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  decreased progressively till the end of the shower in all the 5 events. However, the  $\text{H}^+$  and  $\text{NO}_3^-$  ion concentrations did not show similar variations. The marked decrease in all ions except  $\text{NO}_3^-$ , was associated with an increase in  $\text{H}^+$  ion concentration. To illustrate this converse relationship between  $\text{H}^+$  and other ions more emphatically, data for all the samples, collected during one of the events on 16 September 1988, are plotted in Fig. 1. The minimum concentration of

Table 1. Chemical composition of individual samples collected sequentially during different rainfall events

Date of event	Sample number	pH	Sp. conduct. ( $\mu\text{S cm}^{-1}$ )	Concentration ( $\mu\text{eq l}^{-1}$ )					
				$\text{SO}_4^{2-}$	$\text{NO}_3^-$	$\text{Na}^+$	$\text{K}^+$	$\text{Ca}^{2+}$	$\text{Mg}^{2+}$
26 July 1988 (11)	1	6.71	3.2	16.7	1.3	6.1	1.0	21.0	5.0
	3	6.19	3.1	8.3	3.2	4.8	0.8	18.5	4.2
	6	6.12	3.0	10.4	2.4	2.6	0.8	10.5	2.5
	9	6.07	2.8	8.3	0.7	1.3	0.5	7.5	2.5
	10	6.08	2.8	8.3	7.3	3.5	0.5	7.5	1.7
13 Sept. 1988 (15)	1	7.04	10.8	47.9	6.8	2.2	1.5	90.5	6.7
	3	6.56	9.8	31.3	10.8	0.9	1.0	62.5	6.7
	7	6.20	5.1	8.3	2.9	0.4	0.3	15.0	1.7
	11	6.05	5.5	4.2	7.9	0.4	0.3	9.5	0.8
	14	6.04	5.1	4.2	7.4	0.4	0.3	10.0	0.8
16 Sept. 1988 (17)	1	6.50	13.1	41.7	12.1	8.7	1.8	64.0	7.5
	4	6.10	9.6	33.3	12.7	6.1	1.3	32.5	4.2
	7	6.04	9.0	16.7	16.1	4.4	0.5	29.5	3.3
	10	5.91	4.3	10.4	12.7	2.6	0.3	12.0	1.7
	15	5.87	4.0	4.2	13.4	2.2	0.3	10.0	1.7
19 Sept. 1988 (13)	1	7.23	15.6	50.0	6.8	13.9	3.9	133.5	14.2
	3	7.00	9.2	43.8	4.7	9.6	2.1	98.0	7.5
	5	6.88	8.9	41.7	8.4	11.3	2.3	89.5	6.7
	8	6.84	8.4	37.6	7.4	6.5	1.3	80.5	4.2
	11	6.83	8.3	27.1	8.4	7.0	1.8	60.0	4.2
29 Sept. 1989 (10)	1	6.73	19.2	62.5	1.9	4.8	2.3	68.0	6.7
	3	6.45	8.4	37.5	6.5	1.7	1.0	26.5	2.5
	5	6.42	7.2	25.0	8.4	1.7	0.5	29.5	2.5
	7	6.35	6.1	16.7	5.5	0.9	0.5	7.0	1.7
	9	6.34	5.8	18.8	16.6	1.7	0.3	22.5	1.7

Figures in brackets indicate total number of samples collected during the event.

$\text{H}^+$  in the initial samples may be due to neutralization of some acids in precipitation by atmospheric particulates which contain alkaline substances in the form of carbonates and oxides (Kasina, 1980; Khemani, 1989). Kasina (1980) also states that the neutralization would be most effective near the ground. This supports the washout behaviour of coarse particles namely  $\text{K}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$  and  $\text{Na}^+$ , observed in the present study.

In order to know the relationship of  $\text{H}^+$  with other ions, the correlation coefficients between  $\text{H}^+$  and  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  were calculated for five events and are given in Table 2. There was consistent significant (95% level) negative correlation between  $\text{H}^+$  and  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$  in four events out of five. Among all the elements, the highest significant (99% level) negative correlation was observed between  $\text{H}^+$  and  $\text{Ca}^{2+}$  in almost all the events.

This indicates that  $\text{Ca}^{2+}$  is having highest buffering capacity in neutralizing  $\text{H}^+$  ion concentration during the initial spell of rainfall. However, the correlation coefficient between  $\text{H}^+$  and  $\text{NO}_3^-$  was positive but weak. The correlation coefficient between  $\text{H}^+$  and  $\text{SO}_4^{2-}$  were negative in 4 events and positive in one event. This aspect is explained in Section 4.

The ionic balance could not be studied since the analysis of the  $\text{NH}_4^+$  and  $\text{Cl}^-$  was not carried out. However, our earlier studies on the chemical composition of rain water at Pune indicated that the contribution of  $\text{NH}_4^+$  was negligible and that of  $\text{Cl}^-$  was substantial (Khemani et al., 1985, 1987, 1989).

### 3.2. Sources of ions in rain

The decreasing trend in the concentrations of  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  observed in shower

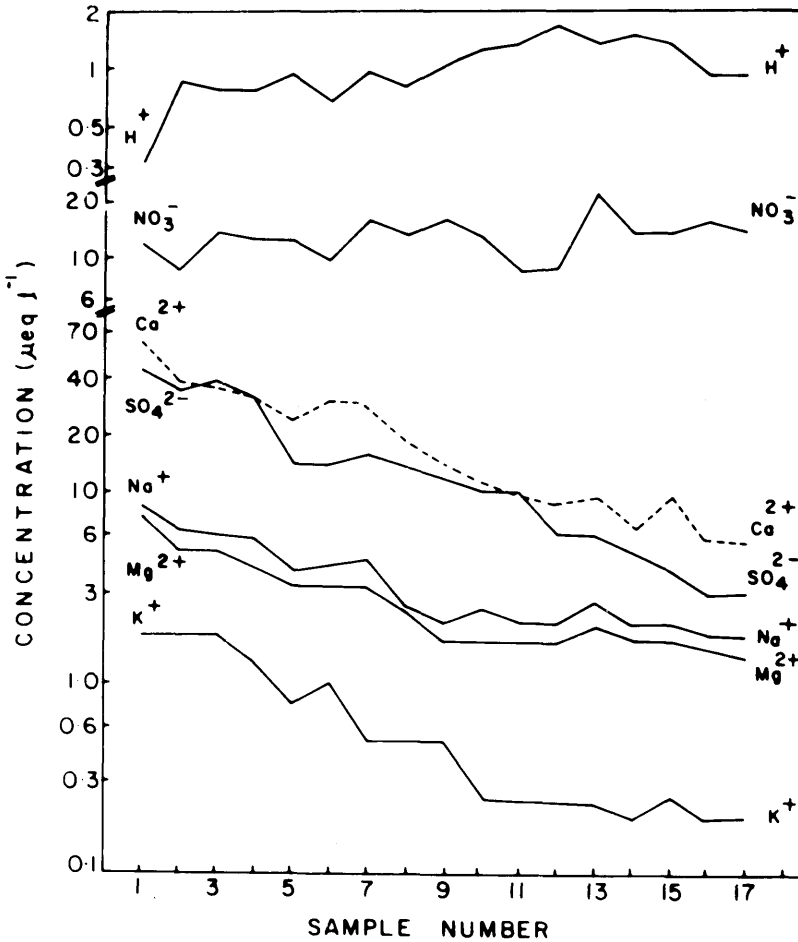


Fig. 1. Variation in the ionic concentrations during a shower event occurred on 16 September 1988.

collected on 16 September 1988 is shown in Fig. 1. Similar trend in the concentrations of these ions was observed in the remaining 4 events but is not shown here. This feature suggests that these elements are uniformly distributed in the airmass and they originate from the same sources. In order to verify their association in rain, correlation coefficients were calculated between  $\text{Ca}^{2+}$  and  $\text{Na}^+$ ,  $\text{Ca}^{2+}$  and  $\text{K}^+$ ,  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$  and  $\text{SO}_4^{2-}$  and  $\text{Ca}^{2+}$  and  $\text{NO}_3^-$  and are given in Table 3. It can be seen that  $\text{Ca}^{2+}$  is significantly correlated with  $\text{Na}^+$ ,  $\text{K}^+$  and  $\text{Mg}^{2+}$  which further confirms that these elements are originating from the same sources (Soil and Sea). This is attributed to wind

blown dust, associated with convection, which is known to be the source of  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Na}^+$  and  $\text{K}^+$  aerosols in the atmosphere. The concentrations of these elements were higher in the initial stage and decreased as the rain advanced. Decrease of these soil-oriented elements in the first few samples were responsible for an increase in  $\text{H}^+$  ion concentration. Out of these elements  $\text{Ca}^{2+}$  plays an important role in neutralisation of  $\text{H}^+$  ion concentration in rain water in India (Khemani, 1992).

Since each sample in the present study has equal volume (0.6 mm), the accumulated rainfall at any sample can be calculated. Simplified washout

Table 2. Correlation coefficient between concentrations of  $H^+$  and  $SO_4^{2-}$ ,  $NO_3^-$ ,  $Na^+$ ,  $K^+$ ,  $Ca^{2+}$ ,  $Mg^{2+}$

Components	Rain number				
	1988			1989	
	1	2	3	1	2
$SO_4^{2-} : H^+$	-0.20* (11)	-0.81 (15)	-0.56 (17)	+0.23* (13)	-0.64 (10)
$NO_3^- : H^+$	+0.43* (11)	-0.60 (15)	+0.04* (17)	+0.28* (13)	+0.11* (10)
$Na^+ : H^+$	-0.69 (11)	-0.66 (15)	-0.62 (17)	-0.51* (13)	-0.71 (10)
$K^+ : H^+$	-0.72 (11)	-0.66 (15)	-0.69 (17)	-0.71 (13)	-0.55* (10)
$Ca^{2+} : H^+$	-0.76 (11)	-0.86 (15)	-0.90 (17)	-0.78 (13)	-0.76 (10)
$Mg^{2+} : H^+$	-0.52* (11)	-0.83 (15)	-0.75 (17)	-0.85 (13)	-0.69 (10)

Figures in brackets indicate total number of samples during the event.

\* Values are not significant. Remaining values are significant at 95% level or more.

Table 3. Correlation coefficient between concentrations of  $Ca^{2+}$  and  $Na^+$ ,  $K^+$ ,  $Mg^{2+}$ ,  $SO_4^{2-}$  and  $NO_3^-$

Components	Rain number				
	1988			1989	
	1	2	3	1	2
$Ca^{2+} : Na^+$	0.66 (11)	0.63 (15)	0.75 (17)	0.77 (13)	0.90 (10)
$Ca^{2+} : K^+$	0.67 (11)	0.72 (15)	0.27* (17)	0.79 (13)	0.88 (10)
$Ca^{2+} : Mg^{2+}$	0.90 (11)	0.99 (15)	0.90 (17)	0.94 (13)	0.89 (10)
$Ca^{2+} : SO_4^{2-}$	0.45* (11)	0.82 (15)	0.75 (17)	-0.04* (13)	0.88 (10)
$Ca^{2+} : NO_3^-$	-0.43* (11)	0.53 (15)	-0.20* (17)	-0.30* (13)	-0.20* (10)

Figures in brackets indicate total number of samples in the event.

\* Values are not significant. Remaining values are significant at 95% level or more.

theory leads to an expectation of component concentration in the air, and therefore in the rain, that decreases exponentially with accumulated rain (Dawson, 1978). In other words, if the natural logarithm of particular component in rain water is negatively related with accumulated rainfall, as seen by the correlation coefficient, it indicates that the particular component is removed by washout mechanism. However, in the case of positive correlation, the particular component may not be removed by washout mechanism. The correlation coefficients were calculated between the natural logarithm of the concentrations of 7 components in each sample of the event and accumulated rainfall up to that sample. Their values are given in Table 4. Although, there is a large variation in the correlation values, the concentrations of  $Na^+$ ,  $K^+$ ,  $Ca^{2+}$ ,  $Mg^{2+}$  and  $SO_4^{2-}$  showed negative relationships with accumulated rainfall (ra). The correlation coefficient between logarithmic concentration of  $Ca^{2+}$  with accumulated rainfall is consistently significant (99% level) in almost all the events. The nss- $Ca^{2+}$  contribution in the rain water samples is between 95 to 98% of the total concentration of  $Ca^{2+}$  values given in Table 1. The mass size distribution of  $Ca^{2+}$  aerosols at Pune has indicated that most of  $Ca^{2+}$  aerosols are in the coarse size mode and soil is the major source of  $Ca^{2+}$  (Khemani, 1989). The results of the present study also indicates that soil is the principal source of  $Ca^{2+}$ . Major source of  $Na^+$  and  $Mg^{2+}$  is the

Table 4. Correlation coefficient between natural logarithm ( $\ln$ ) of component concentration and the accumulated rainfall, ra

Components	Rainfall number				
	1988			1989	
	1	2	3	1	2
$SO_4^{2-} : ra$	-0.28* (11)	-0.58 (15)	-0.96 (17)	-0.34* (13)	-0.85 (10)
$NO_3^- : ra$	+0.61 (11)	-0.31* (15)	+0.36* (17)	+0.55 (13)	+0.72 (10)
$Na^+ : ra$	-0.62 (11)	-0.45* (15)	-0.54 (17)	-0.76 (13)	-0.56* (10)
$K^+ : ra$	-0.54* (11)	-0.76 (15)	-0.74 (17)	-0.71 (13)	-0.65 (10)
$Ca^{2+} : ra$	-0.83 (11)	-0.86 (15)	-0.72 (17)	-0.77 (13)	-0.65 (10)
$Mg^{2+} : ra$	-0.67 (11)	-0.92 (15)	-0.69 (17)	-0.61 (13)	-0.51* (10)
$H^+ : ra$	+0.58 (11)	+0.78 (15)	+0.62 (17)	+0.31* (13)	+0.65 (10)

\* Values or not significant. Remaining values are significant at 95% level or more.

sea. But soil has also been often considered to be the source for  $Mg^{2+}$ ,  $K^+$  and  $Na^+$  (Khemani, 1989). The correlation between  $NO_3^-$  and  $ra$  is positive and significant (95% level) in 3 events, however in the remaining two events the relationship is not significant. This indicates that washout below cloud level may not be important for  $NO_3^-$ . The positive and large correlation of  $H^+$  with  $ra$  in 4 showers suggests an increase of  $H^+$  ion concentrations with an advance of rain.

These results indicate the influence of alkaline aerosol on the chemical composition and pH of rain water and also the preponderance of the washout processes. During the summer monsoon season, the air flow in the lower troposphere is southwesterly and the monsoon current brings inland airmasses from the Arabian sea which are rich in marine aerosol. However, due to afternoon convection, particularly, on days of break-monsoon conditions, the aerosol of soil origin which are highly alkaline are transported into the lower atmosphere. Under such atmospheric conditions the scavenging processes would be predominant due to the dynamical exchange of aerosol of soil origin and continuous supply of fresh aerosols by advection. Earlier studies have indicated that the contribution from natural sources like soil and sea are predominant compared to the industrial sources (Khemani et al., 1987). The present results are consistent with the above studies.

It is surprising to note that the behaviour of  $SO_4^{2-}$  was similar to those of soil-oriented elements ( $Ca^{2+}$ ,  $K^+$ ,  $Na^+$ , and  $Mg^{2+}$ ). This feature indicates that some of the  $SO_4^{2-}$  might have been released from the soil. The sulphate aerosol particles over Pune during the monsoon season have shown bimodal distribution and most of the mass of sulphate was found in the coarse size range (Khemani et al., 1982). Also, correlation coefficient (Table 2) between  $H^+$  and  $SO_4^{2-}$  were negative on 4 out of 5 events and significant (95% level) on 3 events. Negative relationship between  $H^+$  and  $SO_4^{2-}$  (Table 2) and positive relation between  $Ca^{2+}$  and  $SO_4^{2-}$  (Table 3) indicate that most of  $SO_4^{2-}$  is released from the soil. The  $nss-SO_4^{2-}$  values were calculated from the total  $SO_4^{2-}$  values given in Table 1. It was found that the contribution of  $nss-SO_4^{2-}$  is between 92 and 98% of the total  $SO_4^{2-}$  values. Also, correlation coefficients between  $H^+$  and  $nss-SO_4^{2-}$  and  $nss-Ca^{2+}$  and  $nss-SO_4^{2-}$  were calculated and it was

found that correlation values were, by and large, same as given in Tables 2 and 3. The soil has been considered as an important source for sulphate in rain water (Horvath and Meszaros, 1984; Naik et al., 1988). Sequeira (1982) has observed significant association of  $SO_4^{2-}$  with  $Na^+$ ,  $K^+$  and  $Ca^{2+}$  and suggested that  $SO_2$  may be adsorbed onto the particulate matter and react with soil derived  $CaCO_3$ ,  $Na_2CO_3$  and marine derived  $NaCl$  to form the respective sulphate salts. Since large soil derived particles are more rapidly removed by precipitation (Tanaka et al., 1980), the observed rapid decrease of  $SO_4^{2-}$  along with  $Na^+$ ,  $K^+$ ,  $Ca^{2+}$  and  $Mg^{2+}$  due to washout would be expected. The direct relationship between  $H^+$  and  $SO_4^{2-}$  is observed when these ionic components are released from the anthropogenic sources (Castillo et al., 1985).

The variation of  $NO_3^-$  during the shower was entirely different from that of  $SO_4^{2-}$ ,  $Na^+$ ,  $K^+$ ,  $Ca^{2+}$  and  $Mg^{2+}$  (Table 1). This feature indicates that source of  $NO_3^-$  and its removal mechanism may be different from other ions. The removal rates of  $NO_3^-$  in the single shower were examined thoroughly. It was found that in first 20% of the total rainfall of the shower, 50% of total  $SO_4^{2-}$  and only 25% of total  $NO_3^-$  were removed from the shower which occurred on 16 September 1988. This feature suggests that removal rates of  $SO_4^{2-}$  and  $NO_3^-$  are different in the same shower. The removal rates in a shower mainly depend on intensity of rainfall, liquid water content, rain drop size and size of the particles. All the rain water samples collected in the present study have equal volume (0.60 mm) and different duration. Hence the rainfall intensity was calculated for each sample and was grouped into 8 categories, namely, 72, 36, 18, 12, 9, 7.2, 5.5 and 3.8 mm  $h^{-1}$ . The average concentrations of  $Ca^{2+}$ ,  $SO_4^{2-}$  and  $NO_3^-$  were plotted against these rainfall intensities in Figure 2. The concentration of  $Ca^{2+}$  and  $SO_4^{2-}$  decreased along with the intensity rainfall. However,  $NO_3^-$  did not show such variation. This further indicates that washout below the cloud is negligible for  $NO_3^-$ .

Formation of  $NO_3^-$  in the atmosphere may take place through a number of mechanisms. It has been shown that  $NO_2$  reacts with  $O_3$  in the presence of hygroscopic aerosols, such as  $NaCl$  to produce  $NO_3^-$  (Cox, 1974). This mechanism intensifies greatly in a cloud system where the water droplets have a much larger surface area and this

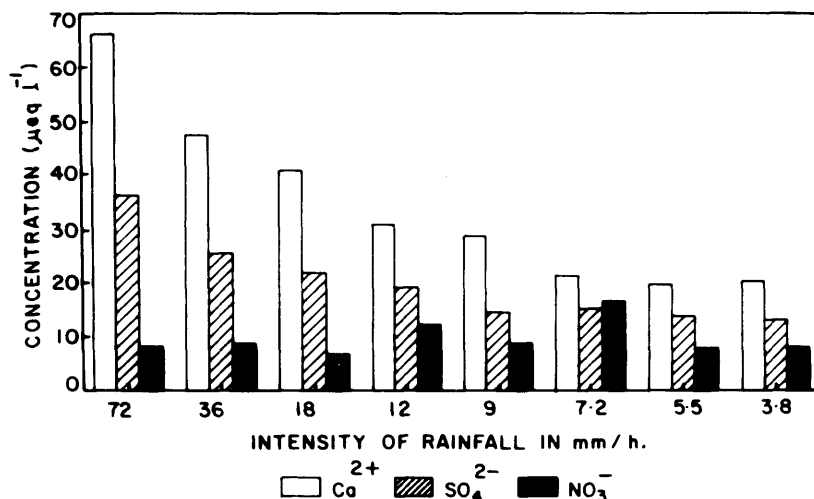


Fig. 2. Variation in the average concentrations of  $\text{Ca}^{2+}$ ,  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$  with rainfall intensities.

leads to  $\text{HNO}_3$  production in the cloud droplets. It has also been shown that  $\text{NO}_3^-$  in rain water may be due to diffusion of nitrogen vapours into cloud drops (Hogan, 1983) forming  $\text{HNO}_3$  on cloud droplets which are, however, buffered by alkaline particulates. Hence, it appears that major contribution of  $\text{NO}_3^-$  in the present study, may be from clouds or rainout processes.

#### 4. Conclusion

The study suggests that short-time sampling within a single precipitation event, compared to bulk sampling for longer duration, used in the

present study appears to give better information about the relationship between  $\text{H}^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$ . The negative relationship between acidity and  $\text{SO}_4^{2-}$  concentration was of special interest and indicates that contribution of industrial  $\text{SO}_4^{2-}$  was negligible.

All components, except  $\text{H}^+$  and  $\text{NO}_3^-$  showed negative correlation between logarithm of concentration and accumulated rainfall lending support to washout mechanisms. The most significant negative correlation was for  $\text{Ca}^{2+}$  and is the major cause for the decrease in pH during a shower, apparently as a result of preferential washout of calcareous soil particles. However,  $\text{NO}_3^-$  ion appeared to be removed by the rainout processes.

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