

## Long term variation in chemical composition of precipitation and wet deposition of major ions at Minicoy and Portblair : Islands in Arabian Sea and Bay of Bengal

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**सार** – इस शोध पत्र में अरब सागर के मिनीकॉय तथा बंगाल की खाड़ी के पोर्टब्लेयर द्वीप के दो स्थानों के वर्ष 1981 से 2002 तक के 22 वर्षों के रासायनिक मिश्रण के केवल आर्द्र-वर्षण आँकड़ों का विश्लेषण किया गया है। विविध आयनिक सकेन्द्रीयकरण के बीच के सहसंबंधों को स्पष्ट करने का प्रयास किया गया है। शरदऋतु के दौरान हुई वर्षा के जल में सल्फेट, नाइट्रेट और हाइड्रोजन आयनों की अधिकतम सान्द्रता पाई गई है। ऋतु वार वर्गीकरण के दौरान मॉनसून ऋतु में सभी आयनों के आर्द्र वर्षण अभिवाह के अधिकतम होने का पता चला है। दोनों ही स्थानों पर अम्लीय निक्षेपण में बढ़ोतरी की प्रवृत्ति देखी गई है। निर्जनद्वीप पर ज्वालामुखी की क्रियाशीलता पोर्टब्लेयर के वर्षाजल में रासायनिक मिश्रण को प्रभावित करती है। सल्फेट आयन ( $\text{SO}_4^{2-}$ ) का वार्षिक आर्द्र वर्षण मिनीकॉय में 15.6 कि.ग्रा. प्रति हेक्टेयर प्रति वर्ष तथा पोर्टब्लेयर में 25.5 कि.ग्रा. प्रति हेक्टेयर प्रति वर्ष पाया गया है तथा नाइट्रेट आयन ( $\text{NO}_3^-$ ) की निक्षेपित मात्रा मिनीकॉय में 38.0 कि.ग्रा. प्रति हेक्टेयर प्रति वर्ष और पोर्टब्लेयर में 74.6 कि.ग्रा. प्रति हेक्टेयर प्रति वर्ष तक पाई गई है। धनायन आयनों में सोडियम आयन ( $\text{Na}^+$ ) तथा कैल्शियम आयन ( $\text{Ca}^{2+}$ ) के तत्व अधिक मात्रा में जमा होते हैं जिनमें मैग्नेशियम आयन ( $\text{Mg}^{2+}$ ) के साथ-साथ पोटेशियम आयन ( $\text{K}^+$ ) भी मिले होते हैं।

**ABSTRACT.** The data on chemical composition of wet only precipitation from two island stations Minicoy in Arabian Sea and Portblair in Bay of Bengal, representing 22 year period, 1981-2002 have been analyzed. An attempt has been made to explain the correlation between various ionic concentrations. The maximum concentrations of sulfate, nitrate and hydrogen ions in rainwater are observed during winter season. When classified by season the wet deposition flux for all the ions is greatest in the monsoon season during which precipitation is substantially high. A tendency for increase in acidic deposition is observed at both the stations. The volcanic activity at Barren island appears to influence the chemical composition of rainwater at Portblair. The annual wet deposition of  $\text{SO}_4^{2-}$  ranged from 15.6  $\text{kg ha}^{-1} \text{yr}^{-1}$  at Minicoy to 25.5  $\text{kg ha}^{-1} \text{yr}^{-1}$  at Portblair, and the corresponding amounts of  $\text{NO}_3^-$  deposited ranged from 38.0  $\text{kg ha}^{-1} \text{yr}^{-1}$  at Minicoy to 74.6  $\text{kg ha}^{-1} \text{yr}^{-1}$  at Portblair. Of the cations  $\text{Na}^+$  and  $\text{Ca}^{2+}$  are the elements deposited in largest quantities followed by  $\text{Mg}^{2+}$  and  $\text{K}^+$ .

**Key words** – pH, Cation, Anion, Wet deposition, GAW.

### 1. Introduction

Sulfur and nitrogen oxides released to the atmosphere, travel hundreds of kilometers from the point of release and mostly get converted into sulfuric and nitric acid under the effect of the solar radiation, humidity and other chemical admixtures (oxidizers, catalyzers) in the air. The average residence times of  $\text{SO}_2$  for different removal and transformation pathways in the atmosphere are as follows: wet deposition 4 days, dry deposition 1-2 days, gas-phase oxidation 10 days and aqueous oxidation 0.5-1.5 days, however, it should be mentioned that there can be large regional and seasonal variations (Moller, 1994). While the lifetime of  $\text{NO}_x$  in the atmospheric boundary layer (about 1 day) is too short to allow transport over long distances, its lifetime in the upper troposphere is of the order of 5-10 days, which is sufficient even for intercontinental transport (Stohl *et al.*,

2002). Precipitation scavenging forms the major pathway for the removal of acidic components from the atmosphere and consequently their impact on the earth's ecosystem. The buffering effects of atmospheric  $\text{CO}_2$  and the soil constituents dictate the final status of the acidic components.

The India Meteorological Department maintains a network of Global Atmosphere Watch (GAW, formerly known as BAPMoN) stations, which has the longest sampling record of precipitation in India. Two island stations of this network namely Minicoy ( $08^\circ 18' \text{N}$ ,  $73^\circ 00' \text{E}$ , 2 m a.m.s.l.) in Arabian sea and Portblair ( $11^\circ 40' \text{N}$ ,  $92^\circ 45' \text{E}$ , 79 m a.m.s.l.) in Bay of Bengal (Fig. 1) have been selected for the present study and provides an evaluation of the results obtained from chemical analyses of monthly precipitation samples, representing 22 year period, 1981-2002. The average annual rainfall of

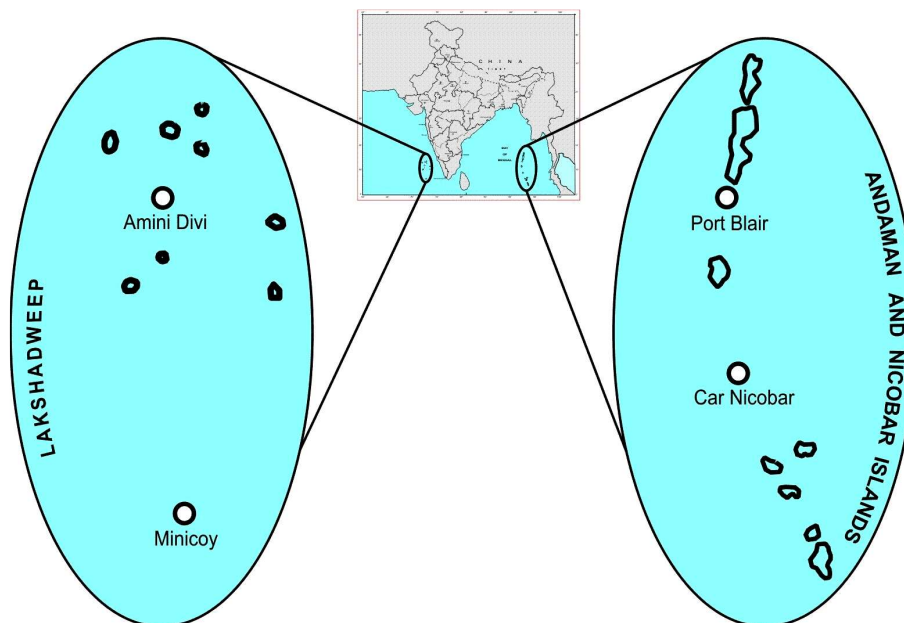


Fig. 1. Geographic map indicating location of islands Minicoy and Portblair

Minicoy is 1676 mm and that of Portblair it is 2894 mm. Approximately 60% of the rainfall is received during south-west monsoon season. The predominant winds during monsoon season at Minicoy are northwesterly to westerly with an average speed of 12 to 16 km/hr, while at Portblair it is southwesterly with an average speed of 14 to 19 km/hr. The winter season is characterized by northerly to northeasterly winds and northerly to northwesterly winds in pre and post-monsoon seasons at Minicoy. Climatological charts showing the wind pattern for Monsoon season for 850 and 700 hPa levels of the atmosphere indicate that air of Arabia, Iran, Somalia and also of Indian origin contribute to the airmass in the Arabian Sea and also in Bay of Bengal. Minicoy has a diesel fired mini power plant in south and a fish-canning industry in west. The area around Portblair is undulating and hilly with open sea towards east. Agriculture forms the major activities in the island.

## 2. Data and methodology

Samples of rainwater were collected in polyethylene funnel (8 inch diameter) attached to polyethylene bottle kept in thermally insulated wooden box to prevent it from sunlight. The funnel is exposed for wet only samples manually at the onset of a precipitation event. While mostly wet precipitation is collected in this way, the contribution of small amount of dry deposition can not be avoided. After each precipitation event the collected water was transferred to a large storage bottle to obtain a monthly sample. The pH and conductivity are measured at

the stations after each event. Samples are refrigerated at 4° C until they are analyzed. Chemical preservatives are not added to the precipitation samples. Monthly samples then transported to chemical laboratory at Pune where samples are analyzed for major chemical components alongwith pH and conductivity using standard methods. The metal ions  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Na}^+$  and  $\text{K}^+$  were determined by Flame Atomic Absorption Spectrophotometry.  $\text{NH}_4^+$ ,  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$  and  $\text{Cl}^-$  ions were determined by UV-Visible Spectrophotometry. The pH, conductivity,  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ ,  $\text{Cl}^-$  and  $\text{NH}_4^+$  data for the period 1981 to 2002 and the cations  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Na}^+$  and  $\text{K}^+$  data for the period 1987 to 2002 have been considered in the present study. Hydrogen ion concentrations were calculated from the pH measurement. The average data of concentration used in this study are based on precipitation-weighted mean values.

## 3. Results and discussion

The precipitation weighted mean concentrations as well as wet deposition flux of anions follow a general pattern of  $\text{Cl}^- > \text{NO}_3^- > \text{SO}_4^{2-}$  and cations follow a pattern of  $\text{Na}^+ > \text{Ca}^{2+} > \text{Mg}^{2+} > \text{K}^+$  (Table 1). At both the stations the sum of major cations is more than that of anions because of which most of the rainwater samples show alkaline pH. In the absence of data for the bicarbonate and organic ion concentrations there could be limitations in assessing the complete ion balance. The sum of anion concentrations is found to be higher at Portblair as compared at Minicoy. Rao *et al.* (1999) found higher concentration of anions in total suspended particulate over Bay of Bengal than that

TABLE 1

Precipitation weighted mean ionic concentration and their standard deviation (in parenthesis) for the period 1987-2002 at Minicoy and Portblair

Ions	Minicoy µeq/L	Portblair µeq/L
H <sup>+</sup>	0.6 (pH= 6.20) (0.2)	4.6 (pH = 5.34) (1.0)
SO <sub>4</sub> <sup>2-</sup>	20.1 (1.9)	17.8 (1.5)
NO <sub>3</sub> <sup>-</sup>	38.6 (5.2)	38.3 (4.5)
Cl <sup>-</sup>	121.7 (10.6)	64.7 (4.9)
NH <sub>4</sub> <sup>+</sup>	13.6 (2.5)	8.7 (1.4)
Ca <sup>2+</sup>	113.8 (8.1)	33.1 (2.8)
Mg <sup>2+</sup>	31.1 (2.6)	16.7 (2.2)
Na <sup>+</sup>	123.8 (9.5)	71.5 (5.3)
K <sup>+</sup>	11.8 (1.0)	11.3 (1.5)

over Arabian Sea. After sea salt, calcium is the major component in the rainwater. Excess calcium in marine aerosols has been reported by several workers (Sequeira and Kelkar, 1978; Khemani *et al.*, 1985; Rao *et al.*, 1999; Kulshrestha *et al.*, 1999). The source region of excess calcium in Indian rainwater, suggested by Sequeira and Kelkar (1978) are Arabia and Iran. Khemani *et al.* (1985) observed excess Ca in marine aerosol near the west coast of India over the Arabian Sea, which is attributed to the transport of soil dust to the west coast of India from the Arabian peninsula.

The annual mean wet deposition of SO<sub>4</sub><sup>2-</sup> ranged from 32.5 meq/m<sup>2</sup>/yr (15.6 kg ha<sup>-1</sup> yr<sup>-1</sup>) at Minicoy to 53.2 meq/m<sup>2</sup>/yr (25.5 kg ha<sup>-1</sup> yr<sup>-1</sup>) at Portblair, and the corresponding amounts of NO<sub>3</sub><sup>-</sup> deposited ranged from 61.3 meq/m<sup>2</sup>/yr (38.0 kg ha<sup>-1</sup> yr<sup>-1</sup>) at Minicoy to 120.3 meq/m<sup>2</sup>/yr (74.6 kg ha<sup>-1</sup> yr<sup>-1</sup>) at Portblair. Among the cations Na<sup>+</sup> and Ca<sup>2+</sup> are the elements deposited in the largest quantity (201 and 184 meq/m<sup>2</sup>/yr at Minicoy and 212 and 93 meq/m<sup>2</sup>/yr respectively at Portblair) followed by Mg<sup>2+</sup> (51 meq/m<sup>2</sup>/yr at Minicoy and 52 meq/m<sup>2</sup>/yr at Portblair) and K<sup>+</sup> (20 meq/m<sup>2</sup>/yr at Minicoy and 34 meq/m<sup>2</sup>/yr at Portblair). Statistical analysis of the pooled data indicated that the differences in annual precipitation weighted mean concentrations of SO<sub>4</sub><sup>2-</sup> and NO<sub>3</sub><sup>-</sup> between Minicoy and Portblair sites are not significant. The higher amounts of SO<sub>4</sub><sup>2-</sup> and NO<sub>3</sub><sup>-</sup> annually deposited in Portblair are due to higher volume of rainfall at this site in comparison to Minicoy. The average annual wet deposition flux of Cl<sup>-</sup> and NH<sub>4</sub><sup>+</sup> does not differ greatly at

the two sites but the concentration of these elements is significantly high at Minicoy.

### 3.1. Stoichiometric ratio and correlation

One measure of the source of the constituent is the comparison of the ratio of the constituent to Na<sup>+</sup> in the precipitation with that in seawater assuming the Na<sup>+</sup> as the reference element of the marine component as opposed to Cl<sup>-</sup>. Although Cl<sup>-</sup> is more abundant in sea salts, it is not always conservative during inland transport of marine salt (Legrand and Delmas, 1988). The ionic ratios show seasonal variation and these ratios do not coincide with those in seawater. The different ion concentrations are plotted against Na<sup>+</sup> (Fig. 2) that aid in identifying the natural sources due to marine aerosols and those with a significant anthropogenic and terrestrial component.

As expected Na<sup>+</sup> and Cl<sup>-</sup> show significant positive correlation (at 5% level) at both the locations. While the average Cl<sup>-</sup>:Na<sup>+</sup> ratios (1.03 for Minicoy and 0.97 for Portblair) are a little lower than that of seawater ratio value of 1.167. In scatter plot of Cl<sup>-</sup> versus Na<sup>+</sup> the slope of the regression line is also different from the seawater ratio. Although the exact mechanism of lower Cl<sup>-</sup> : Na<sup>+</sup> ratio in precipitation is not known, it has been postulated, it involves the loss of chloride in marine aerosol as HCl or Cl<sub>2</sub> by reacting SO<sub>2</sub> or by formation of H<sub>2</sub>SO<sub>4</sub> (Eriksson, 1960) and with NO<sub>2</sub> or by formation of HNO<sub>3</sub> (Green, 1972).

It is clear from Mg<sup>2+</sup>: Na<sup>+</sup> ratio and the correlation coefficient (significant at 5% level) that both the locations receive Na<sup>+</sup> and Mg<sup>2+</sup> from the sea. Although, the average Mg<sup>2+</sup>: Na<sup>+</sup> ratio (0.26 for Minicoy and 0.23 for Portblair) being rather close to that in seawater ratio, 0.226 and its enrichment may not be large but some excess Mg<sup>2+</sup> is indeed present. The ratio of Mg<sup>2+</sup>: Na<sup>+</sup> remains almost constant during all the seasons. In scatter plot of Mg<sup>2+</sup> versus Na<sup>+</sup> (Fig. 2) the slope of the regression line is not significantly different from the seawater ratio but the intercept is significantly different from zero at Minicoy, which suggests that there is a non-sea salt contribution possibly of soil origin. While at Portblair the slope and intercept of the regression line are not significantly different from seawater ratio and zero, respectively suggesting that Mg<sup>2+</sup> originates largely from sea-salt at Portblair.

It is revealed from scatter plot of Ca<sup>2+</sup> and SO<sub>4</sub><sup>2-</sup> versus Na<sup>+</sup> in rainwater (Fig. 2) that both the slope and intercept are significantly different from seawater ratio and zero respectively, suggesting that either fractionation and/ or a variable non-sea salt effect is present. Although, Ca<sup>2+</sup> and K<sup>+</sup> are positively correlated with Na<sup>+</sup> and Cl<sup>-</sup>, the

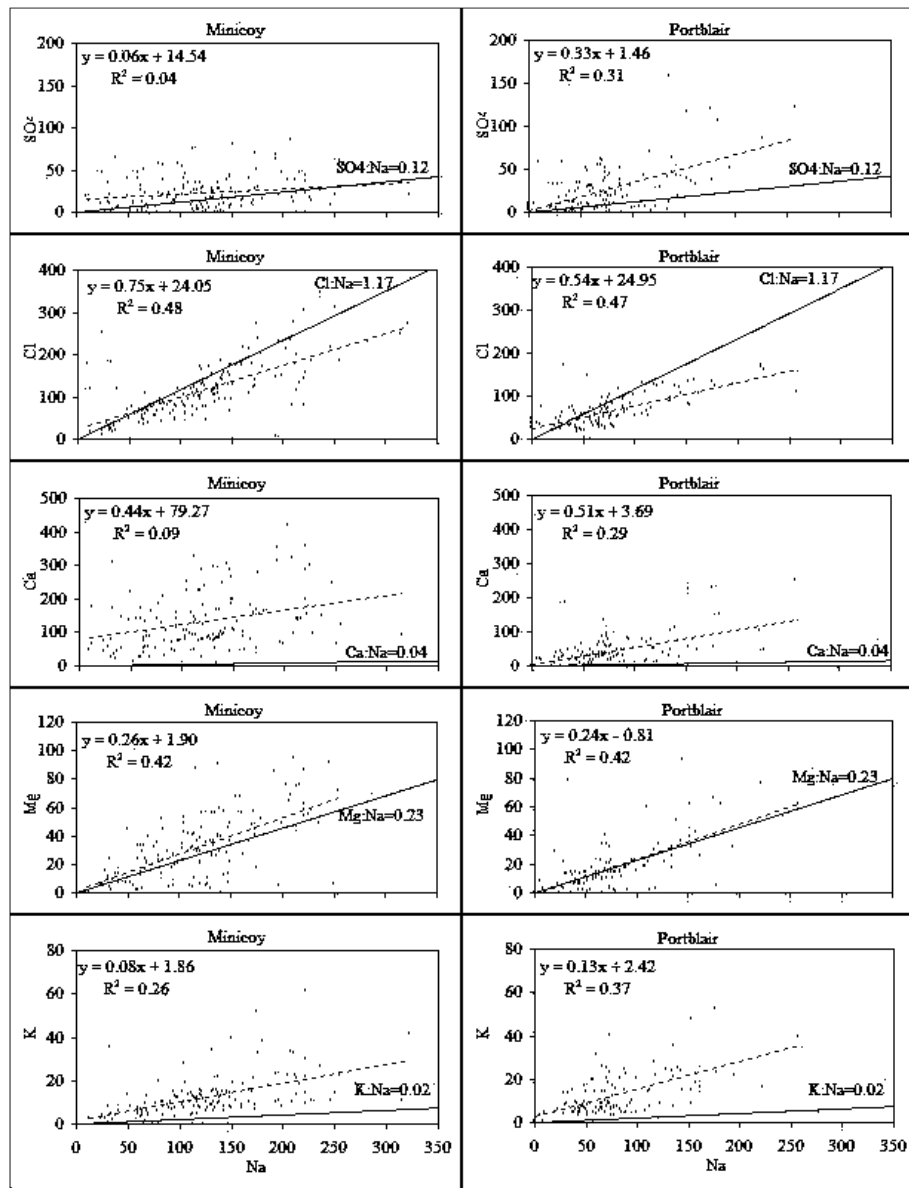


Fig. 2. Scatter diagram between concentration (in μeq/L) of various ions versus concentration of Na. Dotted line represents regression line and solid line is seawater

average Ca<sup>2+</sup>:Na<sup>+</sup> and K<sup>+</sup>: Na<sup>+</sup> ratios are significantly higher in precipitation relative to those from seawater ratio, 0.046 and 0.024 respectively suggesting that the enrichment of these ions with respect to Na<sup>+</sup> are very high. A large scatter in the data above seawater line (Fig. 2) and high enrichment factor with respect to Na<sup>+</sup> suggest that these sites are influenced by sources other than sea also. During monsoon season the Ca<sup>2+</sup>: Na<sup>+</sup> and K<sup>+</sup>: Na<sup>+</sup> ratio are reduced but still much higher than that of seawater ratio. Surprisingly large amounts of Ca<sup>2+</sup>, K<sup>+</sup> and Mg<sup>2+</sup> are found at Minicoy compared to Portblair. During monsoon season wind blown soil particles of local origin may not be the important source for Ca<sup>2+</sup> and K<sup>+</sup>. The excess Ca<sup>2+</sup>

and K<sup>+</sup> in precipitation should largely derive from the long-range transport. Biomass burning is also a source of potassium. Transport of large quantity of dust over Indian Ocean has been well documented. Prospero (1979) observed quite high mineral aerosol concentrations over the Indian Ocean. He suggested that Arabian Sea and to a lesser extent the Bay of Bengal are subjected to a very high input rates of mineral dust. Sources of this dust would be the Arabian peninsula and the arid regions of northern India, the former being the most important. Using "tagged radon" species to track the air masses, Rasch *et al.* (2000) during INDOEX found that in the northern Arabian Sea, most of the air near the surface

TABLE 2

## Interspecies correlation coefficients

	pH	SO <sub>4</sub> <sup>2-</sup>	NO <sub>3</sub> <sup>-</sup>	Cl <sup>-</sup>	NH <sub>4</sub> <sup>+</sup>	Ca <sup>2+</sup>	Mg <sup>2+</sup>	Na <sup>+</sup>	K <sup>+</sup>
<b>Minicoy</b>									
Rainfall	-0.22	-0.24	-0.16	0.02	0.12	-0.36	-0.28	-0.10	-0.23
pH		-0.11	-0.17	-0.09	-0.13	0.36	0.12	-0.02	0.22
SO <sub>4</sub> <sup>2-</sup>			0.33	0.20	0.10	0.31	0.44	0.40	0.20
NO <sub>3</sub> <sup>-</sup>				0.14	0.27	0.10	-0.01	0.13	0.26
Cl <sup>-</sup>					0.05	0.28	0.46	0.72	0.66
NH <sub>4</sub> <sup>+</sup>						0.01	-0.04	-0.02	0.12
Ca <sup>2+</sup>							0.72	0.44	0.64
Mg <sup>2+</sup>								0.78	0.64
Na <sup>+</sup>									0.63
<b>Portblair</b>									
Rainfall	0.12	-0.46	-0.35	-0.23	-0.20	-0.39	-0.22	-0.26	-0.29
pH		-0.07	-0.27	-0.18	0.11	0.02	-0.06	-0.03	-0.10
SO <sub>4</sub> <sup>2-</sup>			0.46	0.59	0.56	0.83	0.69	0.70	0.84
NO <sub>3</sub> <sup>-</sup>				0.21	0.34	0.54	0.21	0.24	0.26
Cl <sup>-</sup>					0.38	0.56	0.62	0.78	0.63
NH <sub>4</sub> <sup>+</sup>						0.41	0.49	0.43	0.59
Ca <sup>2+</sup>							0.64	0.65	0.71
Mg <sup>2+</sup>								0.68	0.74
Na <sup>+</sup>									0.69

originates from Arabia and India and at the higher altitude (2.51 km) air of African origin makes a much larger contribution to the air in the Arabian sea. Krishnamurti *et al.* (1998) also found that the ocean around Indian Peninsula is subjected to the influence of various air trajectories originating from west Asia, Africa and south east Asia besides those from India.

Significant correlation between Ca<sup>2+</sup> and Mg<sup>2+</sup> suggests the common sources for these elements. Concentration of Mg<sup>2+</sup> is much less as compared to Ca<sup>2+</sup> at both the places, this could be due to differential solubility, with Mg<sup>2+</sup> being bound up preferentially in less soluble silicates and Ca<sup>2+</sup> being present as relatively soluble carbonate.

The SO<sub>4</sub><sup>2-</sup> and NO<sub>3</sub><sup>-</sup> show significant positive correlation at Portblair and Minicoy in rainwater samples indicating their common sources. The correlation of SO<sub>4</sub><sup>2-</sup> and NO<sub>3</sub><sup>-</sup> with pH (or H<sup>+</sup>) is non-significant, while nitrate is negatively correlated with pH. It was possible that a fraction of NO<sub>3</sub><sup>-</sup> and SO<sub>4</sub><sup>2-</sup> may be associated with Ca<sup>2+</sup> and Mg<sup>2+</sup> in the form of salts after neutralization process. This was corroborated by significant positive correlation between Ca<sup>2+</sup> and Mg<sup>2+</sup> with NO<sub>3</sub><sup>-</sup> and SO<sub>4</sub><sup>2-</sup> at Portblair (Table 2).

The correlation of SO<sub>4</sub><sup>2-</sup> with Na<sup>+</sup> suggests that it is at least partially of marine origin. The dominant natural sulfur source is the oceanic emission of biogenic sulfur compounds, which constitutes a major portion of the total global atmospheric sulfur burden. The oxidation of biogenic sulfur compounds (H<sub>2</sub>S, Dimethyl sulfide) is the important source of SO<sub>4</sub><sup>2-</sup>. The evaporation of seawater produces many alkali sulfates (*e.g.*, CaSO<sub>4</sub>.2H<sub>2</sub>O, CaSO<sub>4</sub>, Na<sub>2</sub>Ca(SO<sub>4</sub>)<sub>2</sub>, K<sub>2</sub>MgCa<sub>2</sub>(SO<sub>4</sub>).2H<sub>2</sub>O and MgSO<sub>4</sub>.H<sub>2</sub>O). After drops evaporate, the particles form aggregates of loosely attached crystals (Mouri *et al.*, 1993). The significant impact of anthropogenic and non-marine sources on the occurrence of SO<sub>4</sub><sup>2-</sup> concentration in precipitation samples is clearly discernible based on the comparison of the data with SO<sub>4</sub><sup>2-</sup>:Na<sup>+</sup> ratio in seawater. The SO<sub>4</sub><sup>2-</sup>:Na<sup>+</sup> ratio in rainwater (0.24 at Minicoy and 0.36 at Portblair) is very high compared to seawater ratio value of 0.12). The marine contribution to rainwater can be estimated by performing a multivariate regression using sodium (representing marine contribution) and nitrate (for non-marine long-range transport contribution) as predictor variable. Nitrate was chosen, since it is enriched both in dust aerosols and in anthropogenic emissions and since only small amounts of nitrogen are produced from biogenic emissions. Thus the locally produced amount of sulfate can be estimated from the

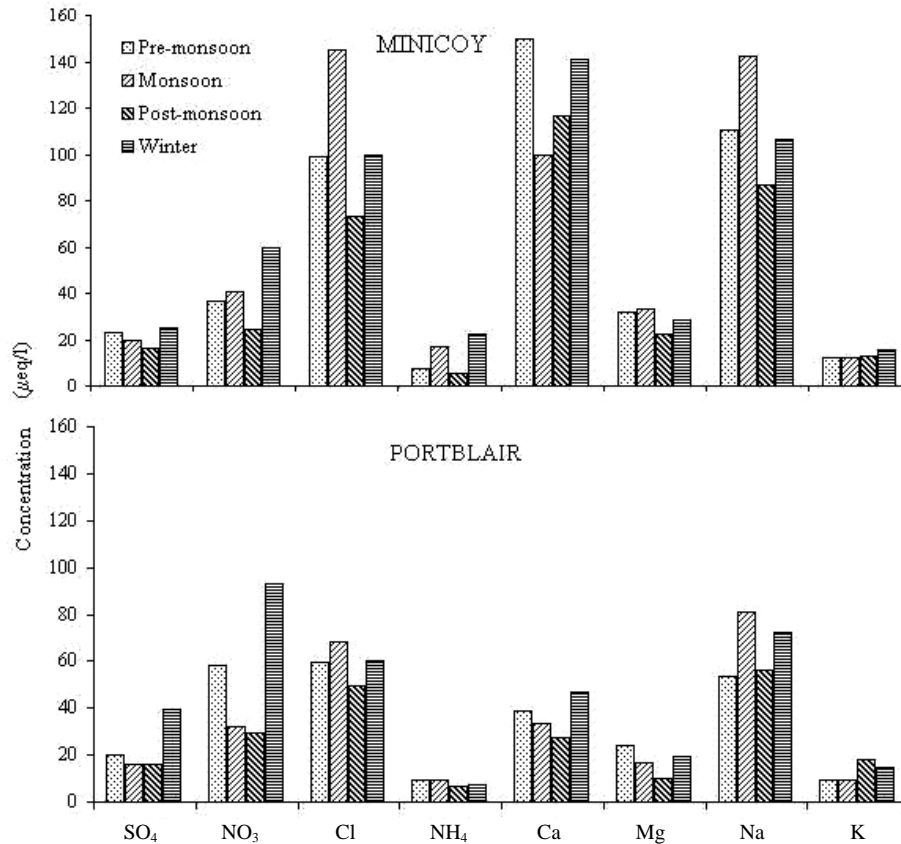


Fig. 3. Precipitation weighted mean ionic concentration ( $\mu\text{eq/L}$ ) by season

multiple regression of sulfate on nitrate and sodium. For Portblair the precipitation weighted multiple regression equation based on 1987-2002 data is :

$$\text{SO}_4^{2-} = (0.142 \pm 0.0015) [\text{NO}_3^-] + (0.121 \pm 0.002) [\text{Na}^+] + (3.73 \pm 0.15)$$

This calculation suggests that the locally produced sulfate (including terrestrial biogenic sulfate) contribute about  $3.73 \pm 0.15 \mu\text{eq/L}$ . Insertion of mean value of nitrate ( $38.3 \mu\text{eq/L}$ ) and sodium ( $71.5 \mu\text{eq/L}$ ) concentration in the above regression equation shows the contribution of non-marine long-range transport component is  $5.45 \pm 0.06 \mu\text{eq/L}$  and marine component is  $8.64 \pm 0.12 \mu\text{eq/L}$  to the sulfate in rainwater. Here, marine component includes both sea-salt and biogenic marine sulfate.

Similarly, for Minicoy the precipitation weighted multiple regression equation is :

$$\text{SO}_4^{2-} = (0.060 \pm 0.002) [\text{NO}_3^-] + (0.071 \pm 0.002) [\text{Na}^+] + (8.92 \pm 0.27)$$

At Minicoy the locally produced sulfate contribute about  $8.92 \pm 0.27 \mu\text{eq/L}$ . The insertion of mean value of nitrate ( $38.6 \mu\text{eq/L}$ ) and sodium ( $123.8 \mu\text{eq/L}$ ) in the above equation suggests that the contribution of non-marine long-range transport component is  $2.31 \pm 0.09 \mu\text{eq/L}$  and marine component is  $8.84 \pm 0.25 \mu\text{eq/L}$ .

The interspecies correlation coefficients are given in Table 2. Most of the species are partially correlated by virtue of negative correlation of each with the amount of rainfall. The linear regression and correlation coefficient of monthly pH values with rainfall amounts shows that pH decreases with increasing rainfall (regression line slope =  $-0.0013$ , intercept =  $7.03$ ) at Minicoy. It can be attributed to the preferential removal of alkaline species or higher amount of acidic precursors in the atmosphere. On the other hand Portblair shows an increase of pH with rainfall (regression line slope =  $0.0005$ , intercept =  $5.77$ ). The high variability of ion concentrations is observed when samples are low. Some of the variability may be due, in part to the length of dry period between rainfall events.

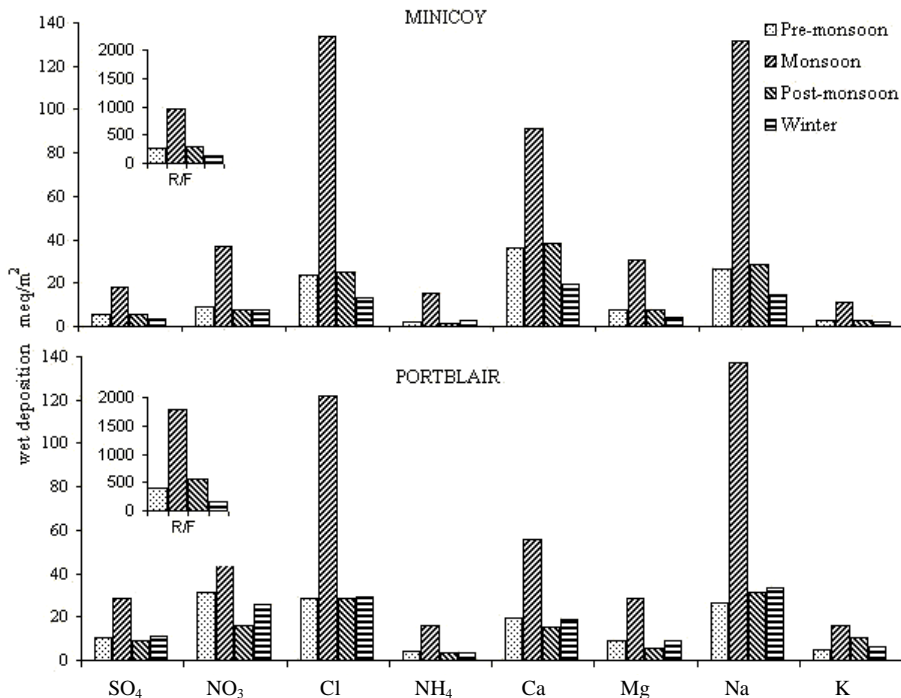


Fig. 4. Rainfall (mm) and mean wet deposition flux ( $\text{meq/m}^2$ ) by season

### 3.2. Comparison between wet and dry season

Winter season includes December through February, pre-monsoon season March to May, monsoon season June to September and post-monsoon season includes October and November. Precipitation is highest in monsoon season and lowest in winter season at both the stations. However, rains over Minicoy and Portblair start in May itself. There was considerable temporal variation between seasons and between years for both ionic concentrations in rainwater and wet depositions. The precipitation weighted mean concentration and wet deposition flux of ions in rainwater for all the seasons are illustrated in Figs. 3 and 4.

Seasonal changes in the acidity of precipitation are illustrated by the fact that the higher precipitation weighted mean hydrogen ion concentrations of  $7.38 \mu\text{eq/L}$  (pH 5.13) at Portblair and  $0.75 \mu\text{eq/L}$  (pH 6.12) at Minicoy occur during the winter season (Table 3). This result is apparently attributed to usually much higher  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$  in rainwater in winter season. Low concentrations of all the ions except  $\text{Na}^+$  and  $\text{Cl}^-$  are observed during monsoon or post monsoon season. However, when the difference in rainfall is considered, wet deposition fluxes are approximately 1.5 to 3 times higher during monsoon season. This must be the result of higher rainfall and more effective advective transport under synoptic conditions of the wet season.

The volcanic activity near Portblair at Barren island also appears to be an obvious candidate for higher  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$  and the lower pH values. Barren island, the only historically active volcano in the region is located about 135 km northeast of Portblair. The first eruption noticed in April 1991 began with hot gases and strong ash emissions with activity continuing through October (Haldar, 1992). Unfortunately, precipitation chemistry data for the year 1991 are not available for Portblair. Another eruption was noticed in December 1994. During January, February and March 1995, thick clouds of pale brownish gas, dark ash particles and white steam were observed. Very high values of sulfate ion concentrations in rainwater were observed from January to April in 1995 (January 159, March 120 and April 107  $\mu\text{eq/L}$ ) when predominant winds are northeasterly. The volcanic emission of smoke was also reported during January, 2000. The pH values show a decreasing and sulfate and nitrate concentrations show an increasing tendency from the year 1995 onwards at Portblair.

The concentrations of  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Na}^+$  and  $\text{K}^+$  have been observed to be significantly higher at Minicoy as compared to Portblair during all the seasons. The concentration of  $\text{Ca}^{2+}$  is 3 to 5 times higher at Minicoy in different seasons. Consequently, the pH values are high at Minicoy as compared to Portblair in all the seasons. The influence of alkaline particulate on acidity of rainwater in

TABLE 3

Precipitation weighted mean ionic concentration ( $\mu\text{eq/L}$ ) and number of samples by season for the period 1987-2002

	Pre-monsoon	Monsoon	Post monsoon	Winter
<b>Minicoy</b>				
pH	6.53	6.16	6.45	6.12
SO <sub>4</sub>	22.9	19.9	16.6	24.9
NO <sub>3</sub>	36.9	40.8	24.6	59.4
Cl	99.1	144.9	73.2	99.5
NH <sub>4</sub>	7.7	17.1	5.5	22.6
Ca	149.8	99.5	116.5	140.7
Mg	32.2	33.3	22.6	28.7
Na	110.2	142.5	86.6	106.2
K	12.5	12.3	13.2	15.3
No. of Samples	47	87	42	41
<b>Portblair</b>				
pH	5.28	5.37	5.32	5.13
SO <sub>4</sub>	19.8	16.4	16.4	39.7
NO <sub>3</sub>	58.4	32.1	29.2	93.4
Cl	59.7	68.5	49.3	60.5
NH <sub>4</sub>	9.4	9.2	6.5	7.5
Ca	38.6	33.7	27.4	46.9
Mg	24.1	16.6	10.2	19.7
Na	53.3	80.7	56.4	72.0
K	9.6	9.4	18.0	14.6
No. of Samples	27	58	26	22

India has been reported by several researchers (Nand, 1986; Khemani, 1987; Varma, 1989; Satsangi, 1998).

The data of the long-term seasonal pattern of the fluxes of Na<sup>+</sup> and Cl<sup>-</sup> with atmospheric precipitation show that these are most substantial during the monsoon season at 137 and 122 meq/m<sup>2</sup> in Portblair and 132 and 133 meq/m<sup>2</sup> respectively in Minicoy. Sodium and chloride deposition patterns differ from those of other species and tend to follow the precipitation pattern more closely. This lack of agreement with other ionic species is expected since Na<sup>+</sup> and Cl<sup>-</sup> are largely derived from sea-salt. During the post-monsoon and winter seasons, low precipitation levels over the station result in the very little wet removal. The wet deposition during post-monsoon or winter season is only 10 to 30% of that of the monsoon season because of low precipitation during these seasons. It is to be mentioned here that rainfall and chemical wet deposition pattern do not agree frequently because of the variability of concentration in precipitation which is a complex function of atmospheric processes, in fact wet deposition patterns are resultant of both rainfall as well as concentration of chemical specie in rainwater.

### 3.3. Long-term trends and decadal variation of chemical composition

The background acidity of precipitation is not only affected by the local environment, but also by the advection of natural and anthropogenic influences from large distances. The presence of high levels of acidity in rain from presumably pristine tropical regions has been observed by several authors (Galloway *et al.*, 1982; Keene *et al.*, 1983; Lacaux *et al.*, 1987; Rao *et al.*, 1995; Freydier, 1998; Morales *et al.*, 1998; Ayers, 2000).

Annual precipitation weighted mean pH values at Minicoy were between 5.43 and 7.42, while individual samples reaching as low as pH 5.06. The annual precipitation weighted mean pH values at Portblair ranged from 4.72 to 6.58 while individual samples reaching as low as 4.25. The frequency of occurrence of histograms of pH for the two decades 1981-1990 and 1991-2000 are presented in Fig. 5. Minicoy and Portblair show an increasing bias towards lower values of pH although broadly retaining the shapes of the distribution. At Portblair the number of samples having pH<5.0 have been



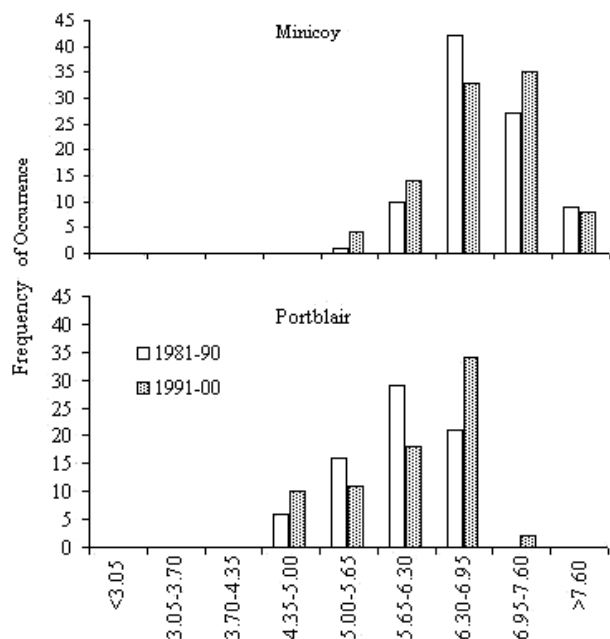


Fig. 5. Frequency of occurrence histogram of pH for two consecutive decades 1981-1990 and 1991-2000

increased, simultaneously the number of samples having  $\text{pH} > 6.8$  also increased keeping the mean pH almost same during both the decades. At Minicoy decadal precipitation weighted mean pH value has decreased from 6.55 to 6.20.

It is observed that pH values at Minicoy were showing an upward trend upto 1991 after that pH values decreased only to rise again from 1996. The overall time trends for pH are statistically non-significant for Minicoy and Portblair. Nevertheless, it may be stated that a slight decreasing tendency for pH is detected at both the places for the period of observation. The increase in hydrogen ion concentration at Minicoy appears to originate from the observed increase of the nitrate and sulfate concentrations. The 22-year annual precipitation weighted mean data series from both the stations reveals an increasing trend in the concentration of sulfate and nitrate. As no time trend is observed for rainfall at the two stations, trends for the wet deposition flux are similar to that of the ionic concentrations.

The mean values of concentration of ions for the two consecutive decades are presented in Fig. 6. The mean values of  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$  and  $\text{H}^+$  ion concentrations during the decade 1981-1990 were 10.5, 12.8 and 0.28  $\mu\text{eq/L}$  respectively which increased to 22.2, 49.0 and 0.63  $\mu\text{eq/L}$  during the decade 1991-2000 at Minicoy. At Portblair the  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$  and  $\text{H}^+$  ion concentrations increased from 11.2, 19.4 and 2.1  $\mu\text{eq/L}$  in decade 1981-1990 to 20.9, 44.7 and 3.8  $\mu\text{eq/L}$  in later decade but  $\text{NH}_4^+$  ion concentration remained almost same during both the decades.

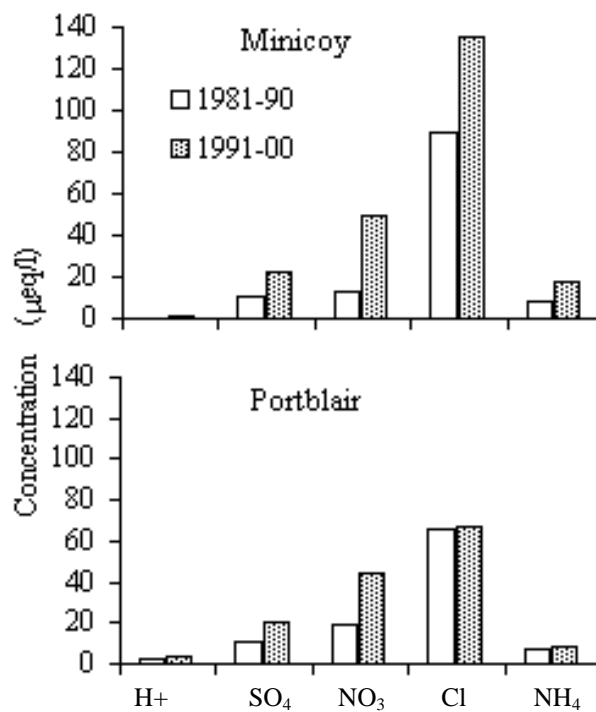


Fig. 6. Change in the precipitation weighted mean ionic concentration ( $\mu\text{eq/L}$ ) and pH during the two consecutive decades 1981-1990 and 1991-2000

#### 4. Conclusions

The precipitation chemistry data over two island stations Minicoy in Arabian Sea and Portblair in Bay of Bengal show the influence of three different source components: marine aerosol, biogenic emissions and a third component, which has characteristics of both soil dust and anthropogenic pollution. Marine aerosols contribute enough  $\text{Na}^+$  and  $\text{Cl}^-$  to make these ions the most abundant cation and anion respectively at the island stations. The analyses of the interspecies correlation, regression analyses as well as stoichiometric ratios suggest strongly the importance of long range transport of soil dust and anthropogenic pollution as the probable cause of the variability of some chemical constituents of rainwater at both the stations. Multivariate analysis shows that a large fraction of the sulfate content of wet precipitation appears to be of marine origin; here both sea salt and biogenic marine sulfur contribute. The non-marine long-range transport component also contributes significantly to sulfate in the precipitation.

A significant amount of chemical species is deposited *via* rainfall at both the places. The wet deposition flux of all the chemical species are approximately 1.5 to 3 times higher during monsoon season. During the post-monsoon and winter seasons, low precipitation levels over the station result in the very little

wet deposition. The monsoon season manifested average lower acidity than the other relatively dry seasons. The low pH values at Portblair are however the result of low alkalinity in precipitation. The 22-year annual precipitation weighted mean data series from both the stations reveals an increasing trend in the concentration of sulfate and nitrate.

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