Mausam, (1979), 30, 4, 449-456

551.510.41 : 551.553.21 (267)

Trace elements in monsoon rains at Bombay and over the Arabian Sea

S. SADASIVAN

Bhabha Atomic Research Centre, Bombay

(*Received 24 June 1978*)

ABSTRACT. A large number of rainwater samples were collected at three locations in Bombay city and analysed for sodium, chlorine, bromine, iodine, manganese, calcium, magnesium and potassium. A few rainwater samples were also collected on board a ship, over the Arabian Sea, and analysed. The results show that the seasalt aerosols predominate the trace element composition of the rainwater. Effect of industrial pollution is localised. The average Cl/Na ratio for all samples is near the seawater ratio of 1.8 while Br and I show respectively a small and a very large enrichment relative to Na from seawater. The results indicate that K is enriched in the transfer from seawater to air while Mg is not. Large Ca excesses are measured in the samples and a need for a correct evaluation of the source of this excess Ca is indicated.

1. Introduction

Seasalt particles are the single major source of atmospheric aerosols and they comprise the major fraction of aerosol mass in marine atmosphere. The chemical composition of rainwater collected at the west coast of India and over the Arabian Sea during southwest monsoon will hence be strongly influenced by the marine aerosol composition. An investigation of the trace elements in such rainwater samples will help in studying sea to air exchange process, monsoonal deposition of seasalt etc. Sampling at urban areas will also aid in an understanding of the effect of urban pollution on rainwater composition. Some of these aspects were investigated by collecting and analysing a large number of rainwater samples from a network of three stations in Bombay city during the 1973 monsoon season. The samples were analysed by neutron activation analysis and atomic absorption spectrophotometry for sodium, chlorine, bromine, iodine, manganese, calcium, magnesium and potassium.

Rainwater composition measurements in India have not been exhaustive and it is only in the last ten years or so concentration of all major inorganic constituents in rainwater were reported (Khemani and Ramana Murty 1968; Handa 1968, 1969 a and 1969 b). However there are no reported estimations of the halogens bromine and iodine. The study of the halogens Cl, Br and I in marine aerosols and precipitation is interesting because of their presence in gaseous and particulate forms and in the case of iodine, due to its known high enrichment, relative to sodium in rainwater, in marine atmosphere. Enrichment, *E*, is defined (Duce *et al.* 1972):

$$E = [\,(X/\text{Na})_{\text{atm.}} / (X/\text{Na})_{\text{seawater}}\,]^{-1}$$

where $(X/\text{Na})_{\text{atm.}}$ is the weight ratio in the sample of element X to sodium and $(X/\text{Na})_{\text{seawater}}$ is the same element weight ratio in seawater. Use of sensitive neutron activation analysis method has enabled, in the present work, the estimation of Br and I in addition to Na, Cl and Mn. In this paper concentration of Na, Cl, Br, I, Mn, Ca, Mg and K in over hundred rainwater samples collected in Bombay city and also that of a few samples collected over the Arabian Sea are presented and discussed.

2. Sample collection and analysis procedure

The locations of the sampling sites in Bombay city are shown in Fig. 1. The first site (Site I) was inside this Research Centre and the second (Site II) was at the top of Trombay hill (305 m) adjoining the Centre. Fertiliser, petroleum and chemical industries are located on the other side of the Trombay hill. Samples were also collected at the Colaba Meteorological Centre's building terrace (Site III). A few samples were also collected on board ship participating in the Indo-Soviet Monsoon Experiment, in the first week of July 1973. These samples were collected along 20° N (Bombay latitude 18° 57′ N) and at distances ranging from 10 km to 600 km from the Indian coast.

Polythene funnel with a 20 cm diameter at top and attached to a polythene bottle served as the collection vessel. The entire collection vessel was thoroughly cleansed with warm dilute nitric acid and rinsed with double distilled water before use. For sampling on board ship the polythene funnel was mounted on a frame which was clamped to a post

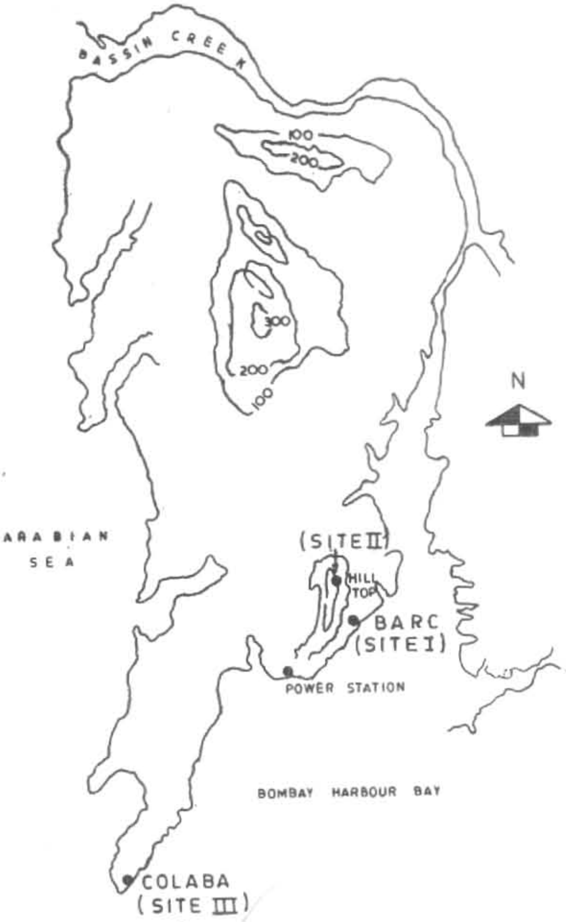

Fig. 1. Map showing the sampling locations at BARC (Site I), Hill Top (Site II) and Colaba Observatory (Site III)

on the ship deck. The funnel level was approximately 9 m above water level and 2 m inside from the railings. A large diameter polythene tubing connected the funnel to the collector bottle that was kept inside a room on the deck. On termination of collection, sample was filtered using a coarse filter and stored in pretreated polythene bottles.

Rainwater sampling was done daily at Sites I and II at 0830 and 1000 hr usually. At Site III the sampling was done twice daily at 0830 and 1730 hr. Samples were collected at Site I from 3 July to 12 August, at Site II from 9 July to 12 August and at Site III during the period 7 July to 11 August. Nearly 40 per cent of season's (June-September) rainfall occurs during July. The winds at the coast are mainly WSW to west (Rao 1976). Rainfall amount for individual collections varied from 0.3 mm to 153.0 mm and the total rainfall amount for the respective durations of sampling at Sites I, II and III were 950.3, 632.1 and 547.6 mm.

The samples were analysed by neutron activation for Na, Cl, Mn, Br and I. The first three elements were measured by instrumental neutron activation analysis (INAA) while post-irradiation chemistry and beta counting was employed for Br and I. Ca, Mg and K were determined by atomic absorption spectrophotometry. The seawater reference element Na was estimated by atomic absorption spectrophotometry (AAS) also. In Table 1 the sodium concentration in some samples determined by both these methods are presented and it is seen that the values generally agree very well. Complete description of sampling and analysis procedures is found elsewhere (Sadasivan 1977).

TABLE 1

Sodium in rainwater samples determined by I.N.A.A. and A.A. Spectrometry

Sample No.	Na (ug/ml) analysed by		Sample No.	Na (ug/ml) analysed by	
	I.N.A.A.	A.A.S.		I.N.A.A.	A.A.S.
150	1.9±0.3	1.6	171	9.9±0.9	8.5
151	0.9±0.1	1.0	172	7.9±0.7	5.8
152	2·6±0·3	2·3	174	14.5±1.2	14.8
153	2.5±0.2	1.7	175	4.1±0.4	3.5
154	4.0±0.4	4.1	176	5.1±0.6	5.1
155	3.1±0.3	4.7	177	5.0±0.5	5.6
156	4.5±0.3	2.1	178	4.7±0.4	4.7
160	7.6±0.6	6.3	179	2.4±0.3	2.0
161	3.0±0.2	3.8	180	1.5±0.2	1.0
162	10.4±0.7	10.9	181	1.9±0.3	1.6
163	7·4+0·6	6·3	182	1.4±0.2	1.4
168	11.6±0.8	10.0	183	1.0±0.1	0.9
169	5.4±0.5	4.9			

3. Results and discussions

The mean concentrations of trace elements in samples from the different sampling sites are given in Table 2. The variation in Cl concentration with Na in the rainwater samples from all four locations is shown in Figs. 2 and 3. Correlation coefficient is over 0.9 for samples from Sites I and III while it is 0.63 for Site II samples. Due to a high Na concentration in one of the five samples from over the sea, a poor correlation is obtained in this case. The Cl/Na values in city samples show large variations, Site III recording the minimum variations and Site II the maximum. Also the mean concentrations in precipitation at Site III are higher than those at the other sampling sites in the city due to the location of the Site III near the tip of the island. It is likely that the concentrations at Site III are

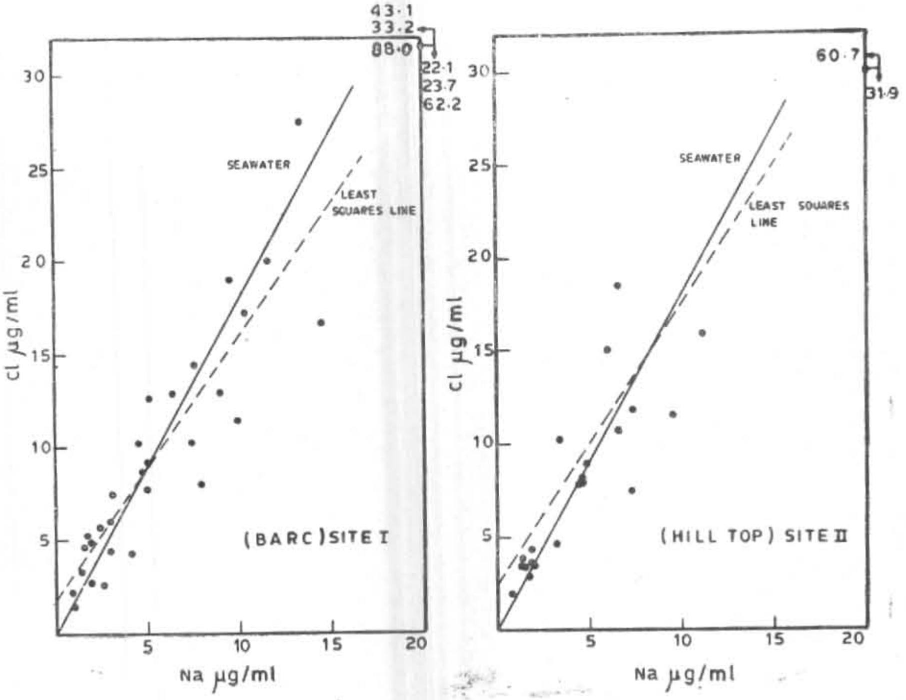

Fig. 2. Plots of chlorine *versus* sodium in rainwater samples

Fig. 3. Plots of chlorine *versus* sodium in rainwater samples

influenced by direct sea spray contamination and washout of giant seasalt particles. The average Cl/Na ratio for all collection sites brackets the seawater ratio of 1.8, in agreement with many other observations reported in literature (*see*, *e.g.*, Junge 1963; Miyake and Tsunogai 1965; Seto *et al.* 1969). The higher individual Cl/Na ratios and poorer Cl to Na correlation in samples from Site II is probably due to dissolution in raindrops of gaseous chlorine that is known to be released from the industries on the other side of the Trombay hill.

Concentrations of Br in precipitation vary from about 10 to 180 ng/ml, excluding a few high concentration samples from Site III. Variation of Br with Na in samples from Sites I and III is shown in Fig. 4 and it is seen that Br in these rainwater samples is derived from seawater only. Most of the points occur to the left of the seawater line indicating an enrichment of Br relative to Na (or Cl) as is also confirmed by the mean ratios in Table 2. Br enrichment is more in the few samples from ship. The measured Br/Cl ratios are in agreement with reported values for marine precipitation (Duce *et al.* 1965; Martens and Harriss 1973) and there does not seem to be any significant amount of Br of pollution origin in these rainwater samples.

Iodine concentrations in the rainwater samples also show wide variations and do not correlate well with the other seawater derived elements. The usually observed I enrichment is noted in all these measurements with samples from Site III and Site I showing similar enrichments, while the few samples from over Arabian Sea show lower enrichment. However the samples from Site II are more

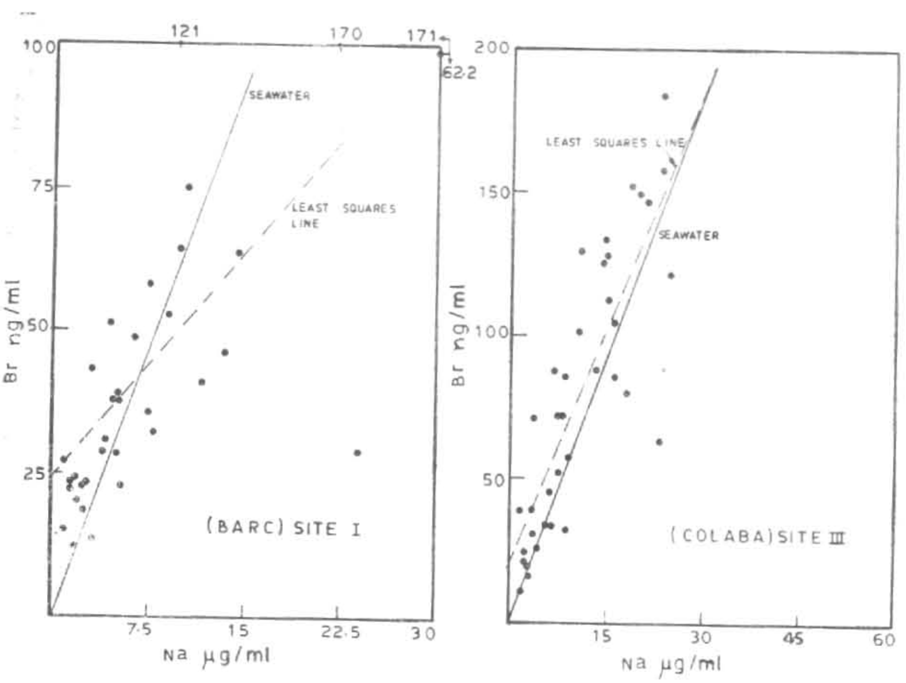

Fig. 4. Variation in bromine concentration with sodium concentration in rainwater samples

TABLE 2

Mean concentration of trace elements in rainwater samples

Element/Ratio*	Site I	Site II	Site III	Ship
Na	3.7 ± 4.2	4.65 ± 2.89	10.7 ± 7.3	4.6 ± 3.9
Cl	7.1 ± 6.7	9.46 ± 6.93	17.1 ± 11.9	6.8 ± 2.8
Mn	32.0 ± 40.8	28.4 ± 19.5	13.2 ± 16.3	23.4 ± 8.06
Br	34.9 ± 24.2	29.3 ± 13.7	79.0 ± 47.9	33.6 ± 33.2
I	15.7 ± 9.4	23.5 ± 10.0	31.6 ± 20.8	13.3 ± 4.7
Ca	2.22 ± 2.52	3.68 ± 2.99	4.3 ± 2.72	1.34 ± 0.94
Mg	1.09 ± 1.19	0.95 ± 0.65	1.28 ± 0.89	0.51 ± 0.34
K	0.47 ± 0.41	0.50 ± 0.29	0.77 ± 0.76	1.02 ± 1.40
Cl/Na	2.05 ± 0.55	2.21 ± 0.94	1.69 ± 0.43	1.82 ± 0.54
Br/Na ($\times 10^3$)	11.42 ± 4.94	9.31 ± 8.72	8.66 ± 4.46	7.0 ± 1.75
I/Na ($\times 10^3$)	5.68 ± 3.48	8.45 ± 6.1	4.63 ± 4.09	3.75 ± 1.91
Br/Cl ($\times 10^3$)	6.34 ± 2.98	4.15 ± 2.99	5.41 ± 3.01	4.59 ± 3.7
I/Cl ($\times 10^3$)	2.97 ± 1.96	3.76 ± 3.92	2.82 ± 2.53	2.14 ± 1.04
I/Br	0.61 ± 0.37	0.90 ± 0.46	0.55 ± 0.51	0.70 ± 0.51

*Mn, Br and I in ng/ml, the rest in ug/ml. The ratio values are the mean of individual ratios.

enriched than at other sites as seen from the I/Na, I/Cl and I/Br ratios given in Table 2.

Average Mn concentration in rainwater samples from the different locations remain within a narrow range, though the values for individual samples vary over a wide range. The mean concentration of ~25-30 ng/ml is higher than the reported concentration in marine precipitations but agrees with the value of 25.3 ng/ml (Bogen 1974) in rainwater samples from Germany. In these (Bogen 1974)

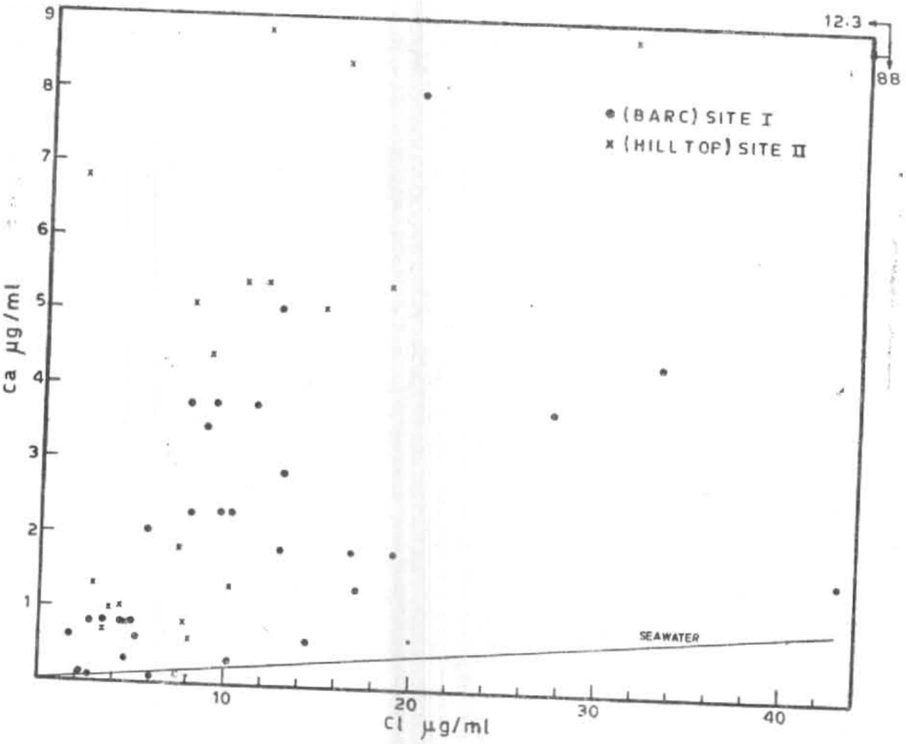

Fig. 5. Ca to Cl in rainwater samples

inland rainwater samples Mn/Na was found to be very close to that obtained in earth's crust while in the present measurements this ratio is very low due to large seasalt contribution.

Significant non-marine origin Ca is observed in the rainwater samples. Ca to Cl variations in the samples are shown in Figs. 5 and 6. The higher slope for Ca *versus* Cl for the samples from Site II is probably the result of industrial processing of large amount of Ca on the other side of the hill. The slopes of regression lines (Ca *vs.* Cl) for Site III and marine precipitation samples is same (0.17) and this value was also obtained for cloud water samples collected at the Ghats, ~60 km inland and not downwind of any industrial belt (Sadasivan 1977). The excess Ca that is measured in the samples is thus seen to have no local origin.

Mg to Cl variations are shown in Figs. 7 and 8. It is seen that for Sites I and II, Mg in the sample is slightly more than that from seasalt alone, possibly due to some local pollution. The correlation between Mg and Cl is very good for samples from Site III and for those from over the sea. The slopes of the regression lines are 0.063 and 0.061 respectively for collections from these two sites. Seawater ratio for Mg/Cl is 0.067 (Culkin and Cox 1966) and it is concluded that Mg in these precipitation samples is derived only from seawater and there is no fractionation in the transfer across sea-air interface.

Potassium correlations with Na or Cl are generally poor and the results indicate K excess for all sampling sites. In Fig. 9 the K to Ca variation in samples from Site III and from over sea are plotted. The seawater line that is drawn can also be taken to represent average soil ratio. Ratio in crustal rock is also indicated in the figure. Excess Ca can be calculated from the Ca to Cl plot and it is 8.1 times the Ca of marine origin for both Site III and marine precipitation samples. Since the average K/Ca seawater and soil ratio is 1.0, the slope of K *vs.* Ca plot corrected for the exess Ca should be 0.12, whereas the slope of this line in Fig. 9 is 0.20. For precipitation over sea, K enrichment is more pronounced, the slope of the regression line being 1.42. K enrichment was also observed in the cloud water samples. Fractionated transfer of K from seawater to air has been proposed to explain the observed values (Sadasivan 1977).

4. Summary and conclusions

The chemical composition of the precipitation in the coastal urban site is similar to that of marine precipitation, specially so if the seawater derived elements only are considered, due to the monsoonal flow with its long travel over the ocean. Effect of industrial pollution seems to be localised, as shown by the composition of rainwater samples from Site II, due possibly to continuous precipitations during the season. The average Cl/Na ratios from the various sampling sites generally

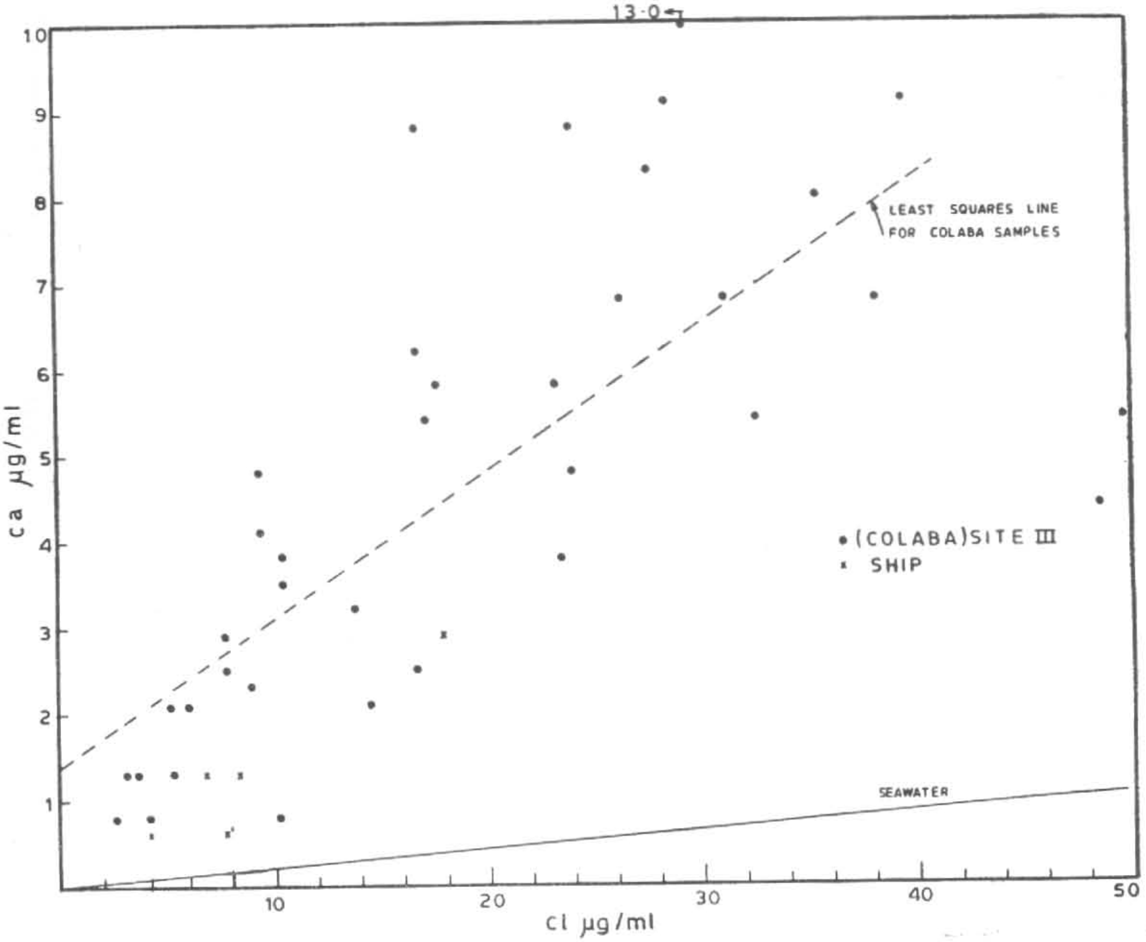

Fig. 6. Ca to Cl in rainwater samples

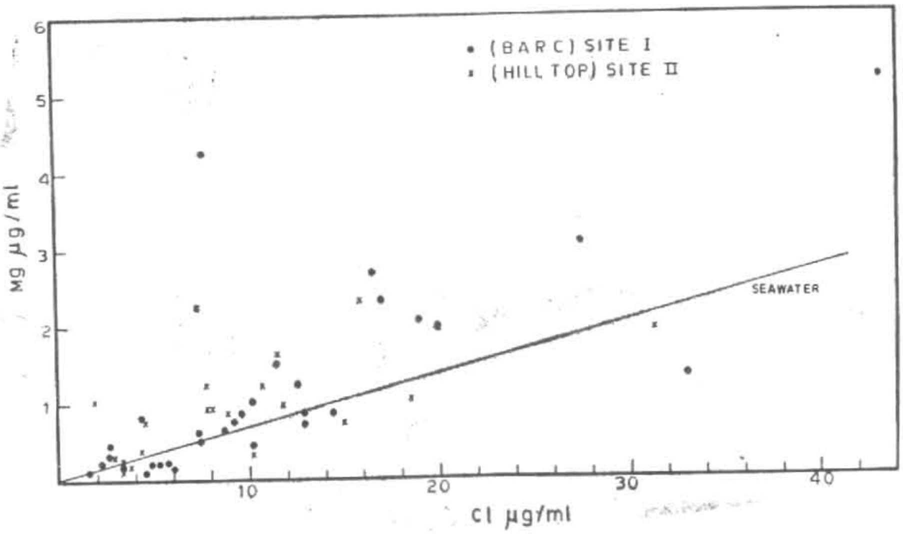

Fig. 7. Variation in Mg concentration with Cl concentration in rainwater samples

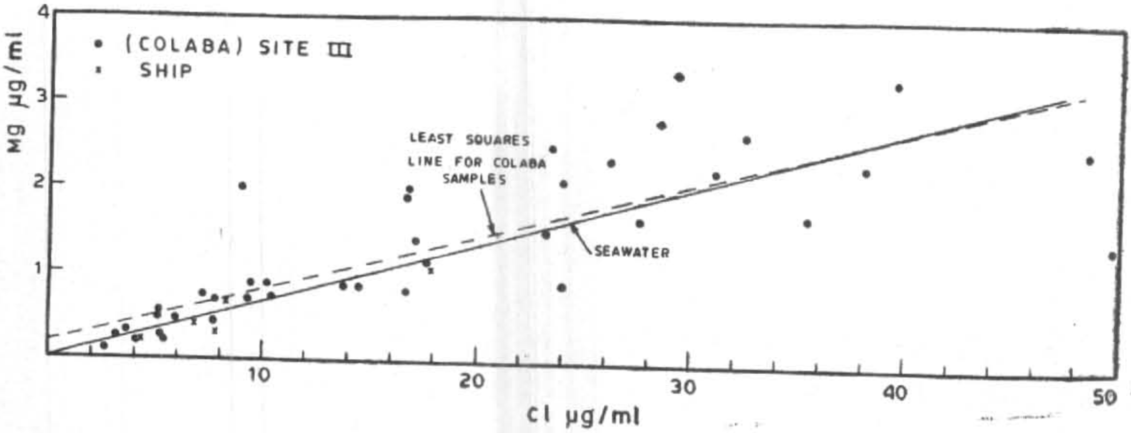

Fig. 8. Variation in Mg concentration with Cl concentration in rainwater samples

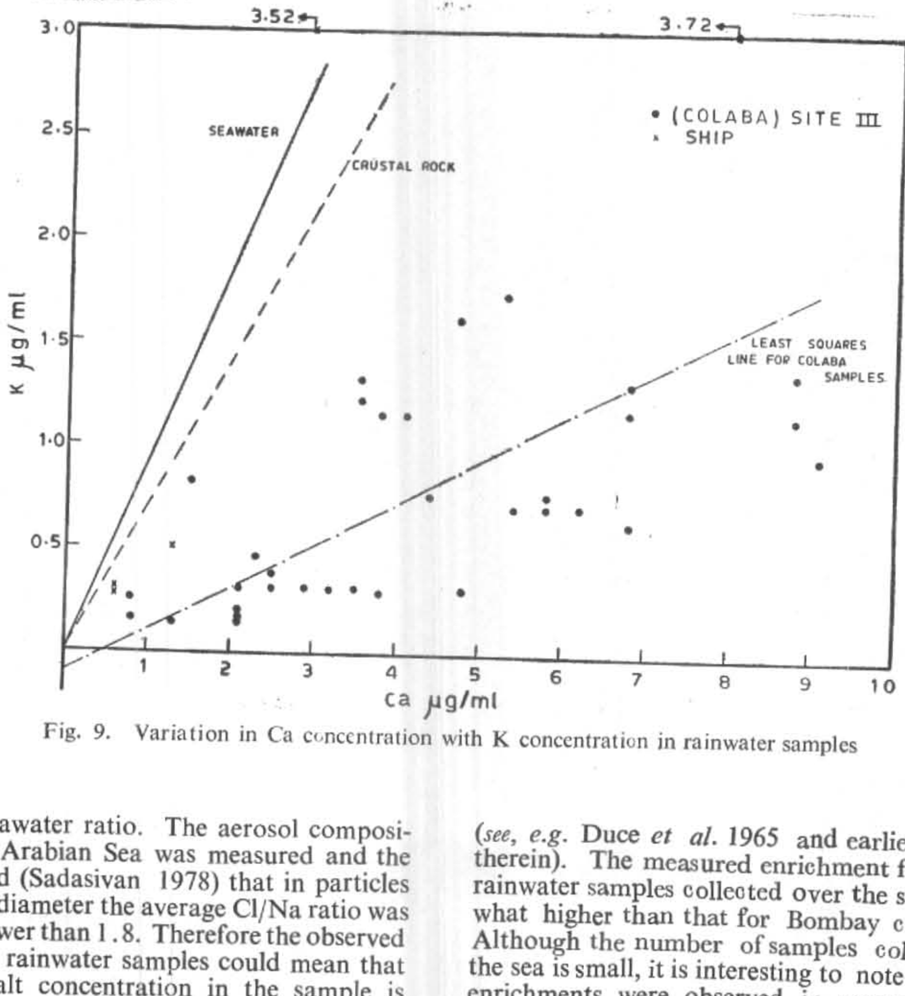

Fig. 9. Variation in Ca concentration with K concentration in rainwater samples

bracket the seawater ratio. The aerosol composition over the Arabian Sea was measured and the results revealed (Sadasivan 1978) that in particles below 0.5 um diameter the average Cl/Na ratio was significantly lower than 1.8. Therefore the observed Cl/Na ratio in rainwater samples could mean that the total seasalt concentration in the sample is largely due to seasalt nuclei of size greater than 0.5 um diameter, namely, the very large and giant nuclei. It is also likely that there is little spatial *separation of* gaseous chloride that is released from seasalt particles (Eriksson 1960). Br in rainwater shows slight enrichment, while I shows considerable enrichment confirming previous measurements (*see, e.g.* Duce *et al.* 1965 and earlier references therein). The measured enrichment for Br in the rainwater samples collected over the sea is somewhat higher than that for Bombay city samples. Although the number of samples collected over the sea is small, it is interesting to note that similar enrichments were observed in aerosols collected over the sea and at the coast (Sadasivan 1977). The enrichment results from a fractionated transfer from the seawater to air and aerosol compositions adequately explain the rainwater compositions. Any contribution to the Br content of rainwater collected at Bombay city from Br of pollution origin is not seen to be significant.

TABLE 3

Ratios of mean concentrations in rainwater samples

Ratio	Seawater ratio	Average soil ratio	This work			Maritime locations Europe (Junge 1963)	Calcutta (Handa 1969 b)	Pune (Khemani 1974)	Delhi (Khemani 1974)
			Over sea	Colaba (Site III)	BARC (Site I)				
Ca/Na	0.038	2.17	0.2	0.4	0.27	0.096	3.27	1.37	4.6
K/Na	0.036	2.6	0.15	0.07	0.06	0.049	0.37	0.31	0.63
Mg/Na	0.12	1.0	0.08	0.12	0.13	0.15	0.50	—	—
Ca/K	1	1.0	1.3	5.6	4.5	1.96	8.8	3.7	7.3

Values for all Indian stations are for sourthwest monsoon rains. Ratios are calculated from mean concentrations

The ratios to Na of Ca, Mg and K and the Ca/K ratio in rainwater samples from present measurements are compared in Table 3 with the ratios in southwest monsoon rainwater samples from three other sites in the country (Handa 1969 b, Khemani 1974). Of the three sites considered, Pune which is ~150 km from Bombay is on the lee side of the Western Ghats. Calcutta is ~50 km from the sea, in the eastern India and Delhi is an inland station. The ratios in rainwater samples from maritime locations in Europe as given by (Junge 1963) as well as the seawater (Mason 1966) and the average soil ratio (Vinogradov 1959) are included in the table. The results show that in rainwater samples no enrichment of Mg in the transfer from seawater to air is observed. As compared to the composition of rainwater at maritime locations in Europe, both Ca and K are in excess in the samples from the present work. The Ca/K value of 1.3 for the few samples from over the sea in the present work is due to high K enrichment and does not reflect the seawater ratio. Ca/K is only slightly higher in rainwater at inland station Delhi than at the coast. Handa (1969b) had explained the observed Ca, K and Mg excesses in rainwater at Calcutta as due to soil origin particles. The Ca/K ratios in the monsoon rains are higher than those observed in the European Air Chemistry network stations (Granat 1972) and indicates high (soluble) Ca in aerosols over the country. It was seen that the measured Ca excesses in samples in the present work is not due to local origin particles. Therefore, it is likely that Ca rich soil particles, like some desertic soils, are responsible for this Ca excess in precipitation samples or else the average soil value is not truly representative in so far as these are related to continental aerosol composition. It is also possible that there is some fractionated transfer of Ca across sea-air interface, although it is not likely to account completely for the measured excesses. A large number of measurements on rainwater at maritime locations indicate Ca excess and it will be worthwhile to pinpoint the source of the calcium.

Acknowledgements

I am thankful to Dr. K.G. Vohra, Head, Division of Radiological Protection and Dr. U.C. Mishra, Head, Air Monitoring Section for guidance and useful discussions. I thank Shri C.R.V. Raman, Deputy Director General, India Meteorological Department, then Director, Regional Meteorological Centre, Colaba for extending to me facilities to collect samples at the Colaba observatory. Thanks are also due to Shri S.J.S. Anand for help in chemical separation.

References

Bogen, J., 1974, *Atmospheric Environment*, **8**, pp. 835-844.

Culkin, F. and Cox, R.A., 1966, *Deep Sea Research*, **13**, pp. 699-705.

Duce, R.A., Winchester, J.W. and Van Nahl, T.W., 1965, *J. geophys. Res.*, **70**, pp. 1775-1799.

Duce, R.A., Stumm, W. and Prospero, J.M., 1972, *J. geophys. Res.*, **77**, pp. 5059-5061.

Eriksson, E., 1960, *Tellus*, **12**, pp. 63-109.

Granat, L., 1972, *Tellus*, **24**, pp. 550-560.

Handa, B.K., 1968, *Indian J. Met. Geophys.*, **19**, pp. 175-180.

Handa, B.K., 1969(a), *Indian J. Met. Geophys.*, **20**, pp. 145-148.

Handa, B.K., 1969(b), *Tellus*, **21**, pp. 95-100.

Junge, C.E., 1963, *Air Chemistry and Radioactivity*, Academic Press, New York.

Khemani, L.T. and Ramana Murty, Bh. V., 1968, *Tellus*, **20**, pp. 284-292.

Khemani, L.T., 1974, M.Sc. Thesis, University of Bombay.

Martens, C.S. and Harriss, R.C., 1973, *J. geophys. Res.*, **78**, pp. 949-957.

Mason, B., 1966, *Principles of geochemistry*. 3rd edition, Wiley, New York.

Miyake, Y. and Tsungogai, S., 1965, *Proc. Int. Conf. Cloud Physics*, Tokyo and Sapporo, pp. 73-78.

Rao, Y.P., 1976, *Southwest monsoon*, India met. Dep., New Delhi.

Sadasivan, S., 1977, Ph. D. Thesis, University of Bombay.

Sadasivan, S., 1978, Atmospheric Environment, **12**, pp. 1672-1683

Seto, Y.B., Duce, R.A. and Woodcock, A.H., 1969, *J. geophys. Res.*, **74**, pp. 1101-1103.

Vinogradov, A.P., 1959, *The geochemistry of rare and dispersed chemical elements in soils*, 2nd edition, Consultants Bureau, New York.