Measurements of acid rain over Indian Ocean and surface measurements of atmospheric aerosols at New Delhi during INDOEX pre-campaigns

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During INDOEX pre-campaigns held in 1995–96, 1996–97 and FFP 1998, the pH of rainwater over the Indian Ocean was observed to be acidic (pH < 5.6). North of or across the Inter-Tropical Convergence Zone (ITCZ), the acidic pH might be caused by the long-range transport of gaseous pollutants such as SO_2 and NO_2 from the Indian subcontinent as well as east African region. The acidity is believed to be contributed by mainly sulphate which may have been produced during SO_2 oxidation over the ocean or long-distance travelling of submicron size SO_4 aerosols. Non-sea salt (nss) SO_4 and nss Ca were higher near the continent and decreased towards the southern hemisphere.

Measurements of total suspended particulate (TSP) matter during the period coinciding with INDOEX pre-campaign 1996 were done at Delhi and compared with the data obtained from the INDOEX pre-campaign-96. Surface measurements were also carried out at Delhi. The concentration of TSP varied greatly over the Indian Ocean during INDOEX pre-campaign 1996 as compared with Delhi. In addition Ca, Mg, SO_4 and NH_4 dominated at Delhi while Cl, Na and SO_4 dominated over the ocean.

PRECIPITATION chemistry is an intricate result of complex interactions between cloud dynamics and microphysical processes as well as a series of in-cloud and below-cloud atmospheric chemical reactions. The acidity and ion concentrations in rain depend on the source strength of the constituents, their physical corporation into the hydrological system, chemical transformation during cloud formation and below cloud scavenging. By studying geographic and temporal variations of marine rain chemistry, we can improve our knowledge on long-range transport of aerosols and gases from land to the ocean as well as the differentiation of natural and anthropogenic sources.

Atmospheric aerosols play an inevitable role in determining atmospheric processes like radiation transfer, cloud formation and precipitation. Therefore, the study of atmospheric aerosols is vital in assessing the level of air pollution in the atmosphere[1]. Atmospheric aerosols arise from two basic processes: (i) dispersal of materials from the Earth's surface, known as primary aerosols, and (ii) chemical reactions or condensation of atmospheric gases and vapours, known as secondary aerosols. From the dispersal of surface materials, comes two major categories, i.e. sea salt and soil particles. Sea salt aerosol particles are formed by the dispersal of ocean water from the foam of the waves, and the other category from the solid surface of the earth, which is then dispersed due to the effect of wind on rocks and soils. A well-known and familiar example of this process is the formation of dust clouds and storms. In regards to the secondary aerosols they are mainly attributed to anthropogenic sources[2].

In recent years, studies on atmospheric aerosols have gained great importance because of their effects on atmospheric processes and climate, especially submicron-sized aerosols which contribute to the cooling of the atmosphere by scattering of incoming radiation in the atmosphere. The extent of this scattering effect may differ for continental and marine regions depending on the abundance of submicron-sized aerosols.

The present study reports the results of precipitation chemistry during pre-INDOEX campaigns of 1996, 1997 and 1998. A comparative study of chemical composition of aerosols at Delhi (a highly polluted location) and over the Indian Ocean during INDOEX pre-campaign 1996 has also been completed. In this study we assess the atmospheric acidity in the Indian Ocean region along with possible means of transport of SO_2, SO_4 and Ca aerosols. In addition, non-sea salt (nss) fractions of major components of rainwater have been calculated.

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Experimental

Sample collection

Rainwater samples were collected during *Sagar Kanya* cruise # 109, 120 and 133 on the bow deck as well as on bridge deck. The height of the bow from sea surface was around 9 m, while the bridge was around 16 m from the sea surface. These two heights were chosen to ascertain the best location for a contaminationless composition. The samples were collected using automatic wet only collectors at both places which were operated with a remote controller. The samplers were fitted with a 2 l capacity polypropylene bottle and polypropylene funnel 22 cm in diameter. Samples were collected on event basis, then immediately after the event they were brought to the ship laboratory for pH measurements. To prevent biological decay, thymol was added to the samples[3].

Ambient particulate matter was collected with a hi-volume sampler (Envirotech, APM 410). The sampler consists of a vacuum pump, a filter platform, a flow rate meter and an automatic timerset. When air is sucked through the filter, particles coming in with the airstream settle on the filter. EPM 2000 glass fibre filters were used to collect the aerosol particles with the hi-volume sampler. These filters withstand relatively high air flow rates, are high in efficiency without requiring impaction velocity and possess lower humidity sensitivity. A glass fibre filter is the filter of choice for total suspended particulate matter (TSP) measurements and is especially good for solvent extraction.

In Delhi, aerosol samples were collected on the terrace of National Physical Laboratory (NPL) at a height of 1.5 m. The height of the building was 13 m from the ground level. Sampling was carried out for a period of 24 h beginning at 9.30 a.m. in January 1996. The sampler was operated at an average rate of 1.0 m^3 min^{-1}. Before and after sampling, the filters were desiccated to eliminate the effect of humidity (RH < 50%) and weighed to determine the mass of particles. The total mass of TSP deposited during the sampling period was determined gravimetrically. TSP samples were also collected over Indian Ocean with a similar high-volume sampler enroute *Sagar Kanya* cruise # 109 as shown in Figure 1.

Sample preparation and analysis

The extraction from 1″ × 1″ filter paper was made by ultrasonic extractor in 50 ml of deionized water for water soluble components. The samples were preserved with thymol and then refrigerated and analysed. The samples were analysed for Cl, SO_4, NO_3, Na, K, Ca, Mg and NH_4. The anions were analysed by ion chromatography (Dionex 2000i/SP) using Dionex AS4 A column, $Na_2CO_3/NaHCO_3$ eluent and H_2SO_4 as regenerant for cruise # 109, cations were analysed by atomic absorption spectrophotometry, while NH_4 was analysed colorimetrically by indo-phenol method using a UV-visible spectrophotometer[3,4]; for cruise # 120, NH_4 was estimated by flow injection analysis. The analysis of the samples collected during cruise # 109 was performed at NPL, New Delhi, while for cruise # 120 analysis was made at NPL and at the International Meteorological Institute, Stockholm, Sweden.

Results and discussions

Figure 1 is the plot of the cruise tracks for *Sagar Kanya* cruise # 109 (December 1995 to January 1996), # 120

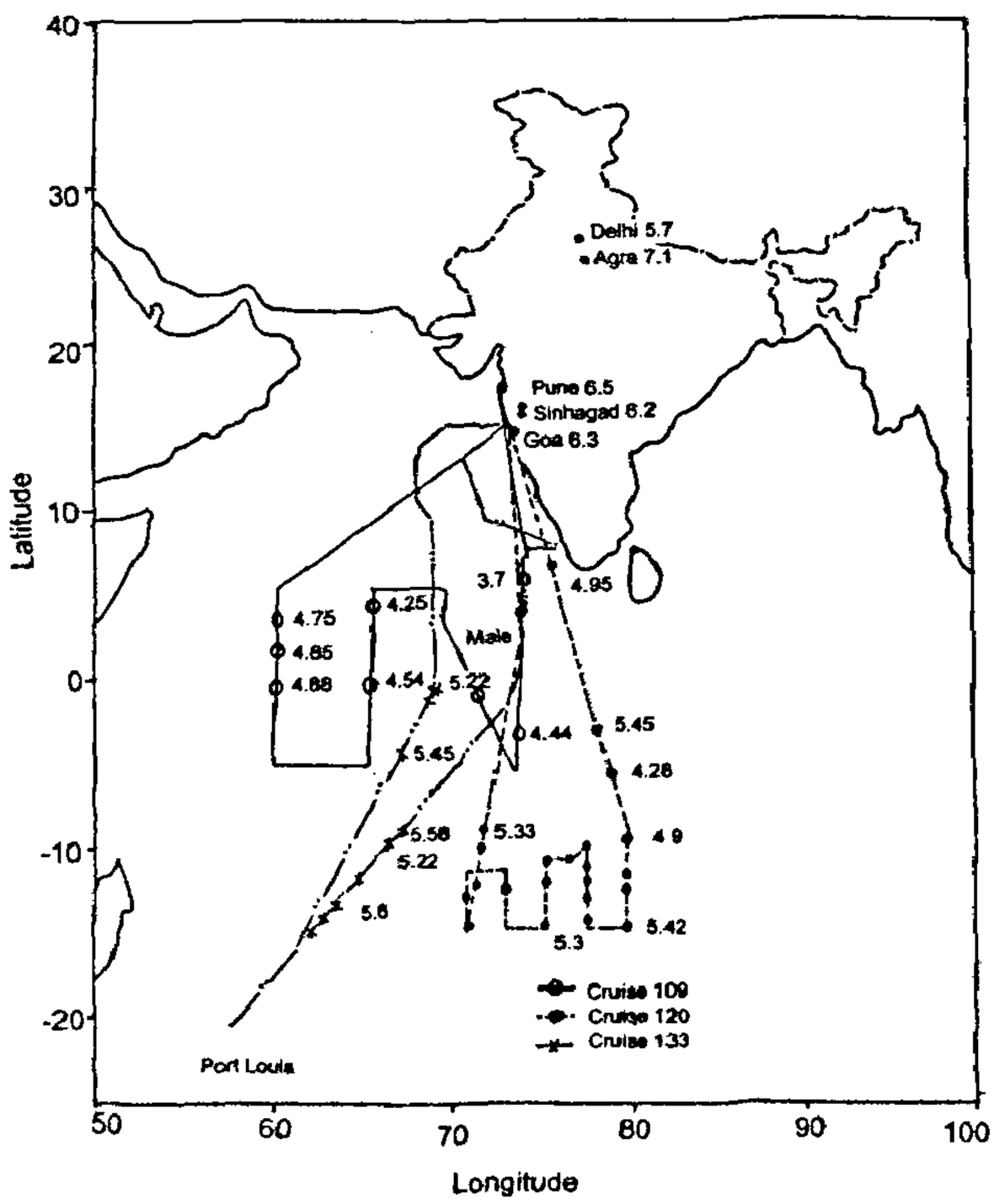

Figure 1. Location of continental sites and cruise tracks for *Sagar Kanya* cruise # 109, # 120 and # 133.

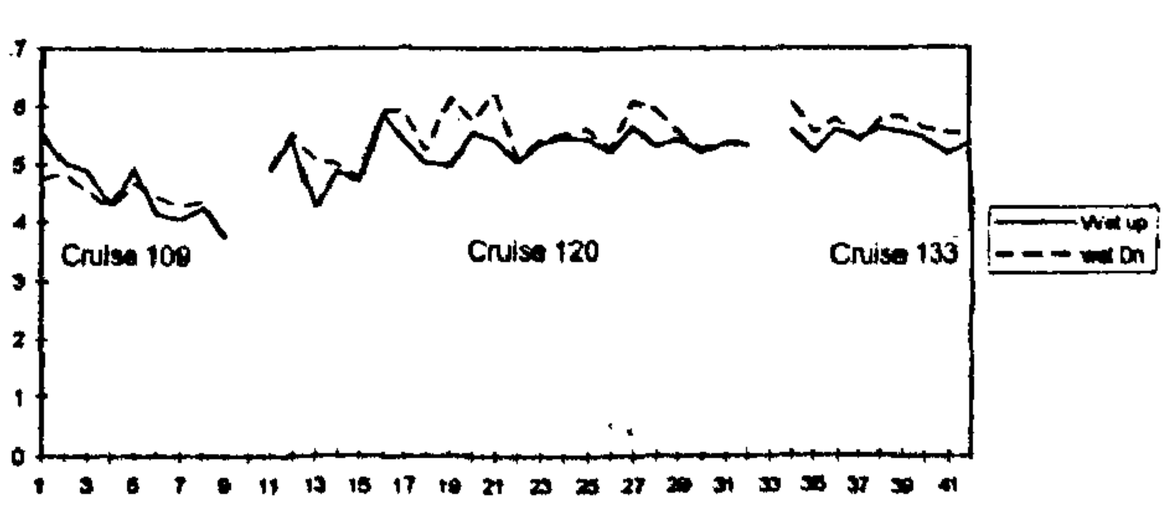

Figure 2. pH of rainwater collected at bow deck (wet down) and bridge deck (wet up).

(January 1997) and # 133 (February to March 1998) along with some continental locations showing their pH of rainwater. We see that a total of 9, 22 and 9 rain events were observed during cruise # 109, 120 and 133 respectively. Out of 22 events during cruise # 120, only 15 were found to have sufficient volume for analysis. The pH values in Figure 2 indicate that the ocean is acidic (below 5.6), while continental sites are highly alkaline, except at Delhi which is a highly polluted site.

Comparison of pH of rainwater at bow and bridge deck

Figure 2 also presents the pH variation of the rainwater collected at the bow (wet down) and bridge deck (wet up). The pH varied in the range 3.75–4.85, 4.28–5.89 and 5.22–6.05 during cruise # 109, 120 and 133 respectively. It is clear from Figure 2 that the pH of rainwater is higher at bow than at the bridge deck. At the bow, the sea salt interference was observed to be very high during rough seas since much sea spray entered the collector, thus interfering significantly with the rainwater composition. Considering this interference on pH and composition of rainwater, we have rejected the bow samples, and only bridge deck samples are discussed here. In addition, only pH values are discussed for cruise # 133 since chemical analysis of the samples is still in progress.

Variation of pH with SO_4

Figure 3 shows the variation of pH and SO_4 during cruise # 109 and 120; clearly, when the SO_4 rises, pH decreases during cruise # 109. However, during cruise # 120, there is no clear indication of this relationship. Moreover, the SO_4 concentrations are much higher during cruise # 109 compared to cruise # 120. This may be due to the difference in the investigated region during the two cruises. For instance, cruise # 109 was closer to the Indian subcontinent which might have contributed by its air masses rich in SO_2 and SO_4. During cruise # 120, the ITCZ was characterized between 7°S and 14°S, and except for only two events, all were observed across ITCZ where air is supposed to be cleaner. The lower range of pH during cruise # 109 is also an indication of higher influence of the subcontinent.

Variation of SO_4, NH_4 and Ca and transport of SO_4 aerosols

Primarily SO_4 in rainwater is associated with NH_4 forming ammonium sulphate. In the present study, we have observed the association of SO_4 with Ca in addition to NH_4 (as seen in Figures 4 and 5) during both the cruises, thus indicating the presence of $CaSO_4$ in the rainwater. The association of SO_4 with NH_4 and Ca might be due to any of the following processes:

(i) Transported SO_2 from the continent is converted into sulphuric acid and combines with atmospheric ammonia forming ammonium sulphate which is removed during the cloud scavenging, thus

$$2NH_3 + H_2SO_4 \rightarrow (NH_4)_2SO_4.$$

(ii) During winter over the continent, SO_2 is oxidized to H_2SO_4 droplets which are absorbed on the surface of the existing crustal particles in the atmosphere. These particles are then transported over the ocean. Abundant sulphuric acid maintains the high acidity even after the association with Ca aerosols. These particles are larger in size owing to the liquid content and, hence, can travel a shorter distance compared to $(NH_4)_2SO_4$ which is crystalline and can travel longer distances. Figures 4 and 5 clearly show that during cruise # 109 the Ca concentra-

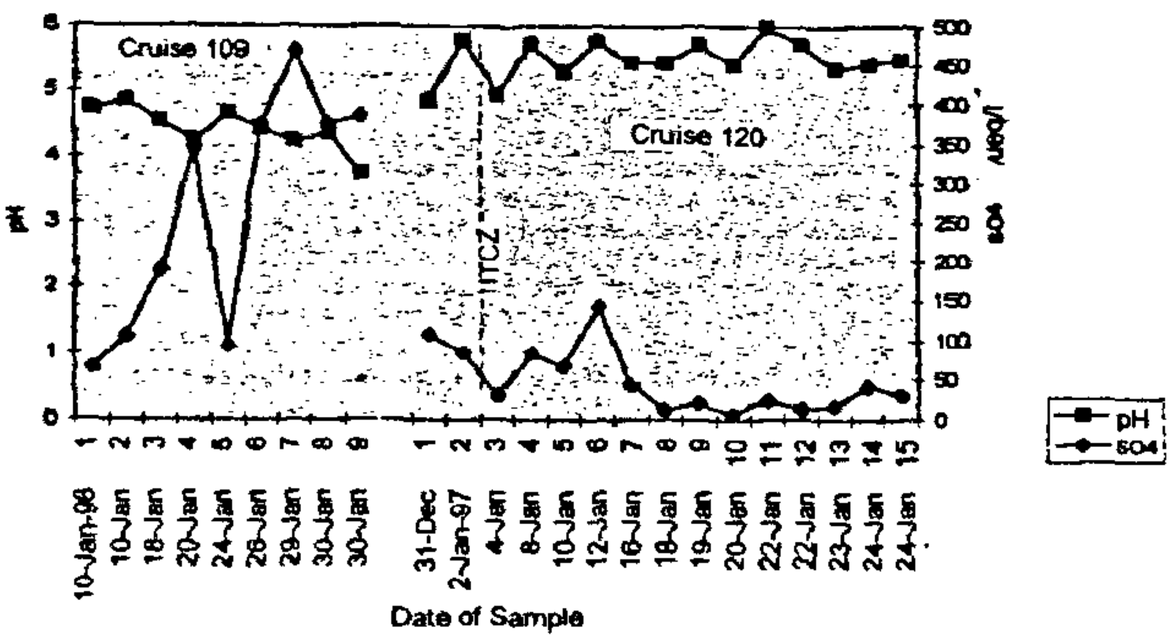

Figure 3. Variation of pH (wet) and SO_4 in rainwater during cruise # 109 and 120.

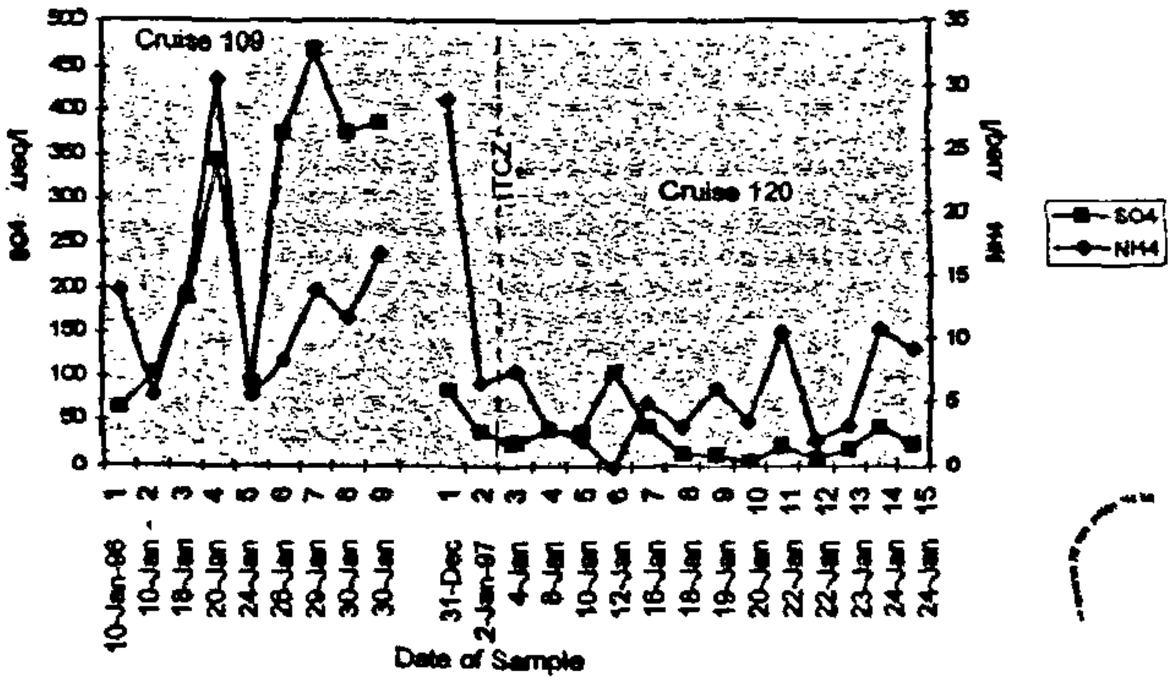

Figure 4. Variation of SO_4 and NH_4 in rainwater during cruise # 109 and 120.

tions are higher up to 90 μeq/l, but during cruise # 120 up to 14°S, Ca concentrations are observed up to 30 μeq/l. On the other hand, NH_4 does not exhibit such a large difference in concentrations during either cruises.

(iii) SO_2 is adsorbed on aerosol particles such as soot, dust or metal oxides, and is oxidized by a catalytic reaction (with Fe and Mn present in significant quantity to activate the reaction). Higher relative humidity enhances the aerosols–SO_2 interactions. SO_2 is further scavenged by clouds and shows association with both Ca and NH_4. Strong correlations were found between the first-rate constant and several metals like Fe and Mn[3]. In the INDOEX samples, the concentrations of Fe and Mn were estimated as 5 μg/l and 1 μg/l respectively, which is sufficient to catalyse the SO_2 oxidation by O_2.

The concentration of TSP is much higher at Delhi than over the Indian Ocean. The concentration of TSP at Delhi varies from 158 to 405 μg m^{-3}, with an average of 294 μg m^{-3}, while it varies from 7 to 54 μg m^{-3}, with an average of 31 μg m^{-3} over the Indian Ocean. A high concentration of TSP at Delhi is due to the crustal as well as anthropogenic contributions. The variations in TSP with latitude for three *SK* cruises appear in Figure 6. As evident from the figure, the TSP concentrations near Male in cruise # 133 during the onward journey were maximum due to anthropogenic activities on Male islands, and thus concentrations decreased sharply after Male. TSP concentrations during cruise # 120 were comparatively higher, especially between 10 and 15°S, which could be caused by a tropical storm effect during that period.

Figure 7 shows major ion concentrations of water soluble components of TSP at Delhi and over the Indian Ocean during January 1996. Ca and Mg, being crustal components, have high loadings in TSP at Delhi. The concentration of SO_4 is also high at Delhi as a result of crustal as well as anthropogenic contribution. Naturally, the concentrations of Na and Cl are higher over the Indian Ocean than at Delhi as Na and Cl are major sea salt components, with concentrations of Ca and Mg higher at Delhi than over Indian Ocean. Though the SO_4 concentration is high at Delhi, Ca and Mg concentrations are much higher than SO_4 concentration which buffers the acidity of rainwater caused by SO_4. On the other hand, over the Indian Ocean, the pH of rainwater is acidic which is mainly due to high concentration of SO_4 and NO_3 components. Ca and Mg concentrations over Indian Ocean are not sufficient to buffer the acidity of rainwater. Possibly the high concentration of SO_4 over the Indian Ocean might have contributed by continental sources as the N–E trade winds prevail during this period.

Contribution from non-marine sources

The influence of non-marine sources has been estimated by calculating nss fractions. Sea salt and nss fractions were calculated assuming Na as reference[4]. Sea salt ratios over the Indian Ocean in rainwater are presented in Table 1 and have been compared with continental sites, viz. Delhi, Goa and Pune. Over the Indian Ocean as well as coastal site Goa, Cl/Na ratios are almost representative of sea water ratio. But for SO_4 and Ca the variation is very large which may be due to the high extent of influence by anthropogenic and crustal sources. Figure 5

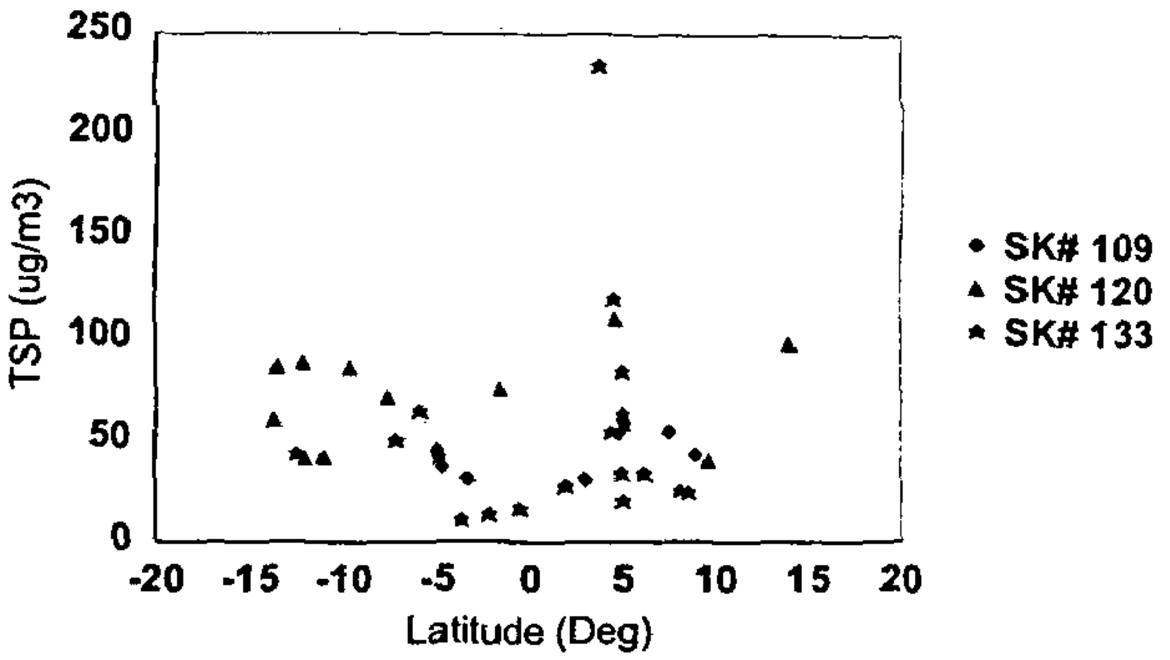

Figure 6. Variation of TSP with latitude over Indian Ocean during cruise # 109, 120 and 133.

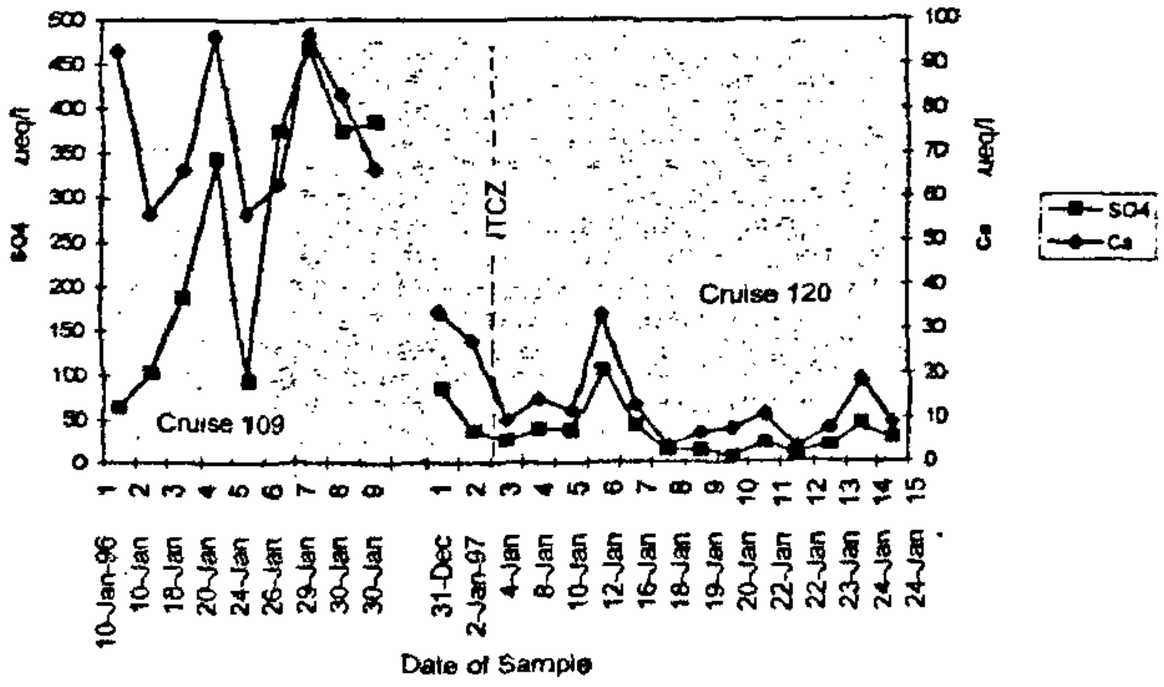

Figure 5. Variation of SO_4 and Ca in rainwater during cruise # 109 and 120.

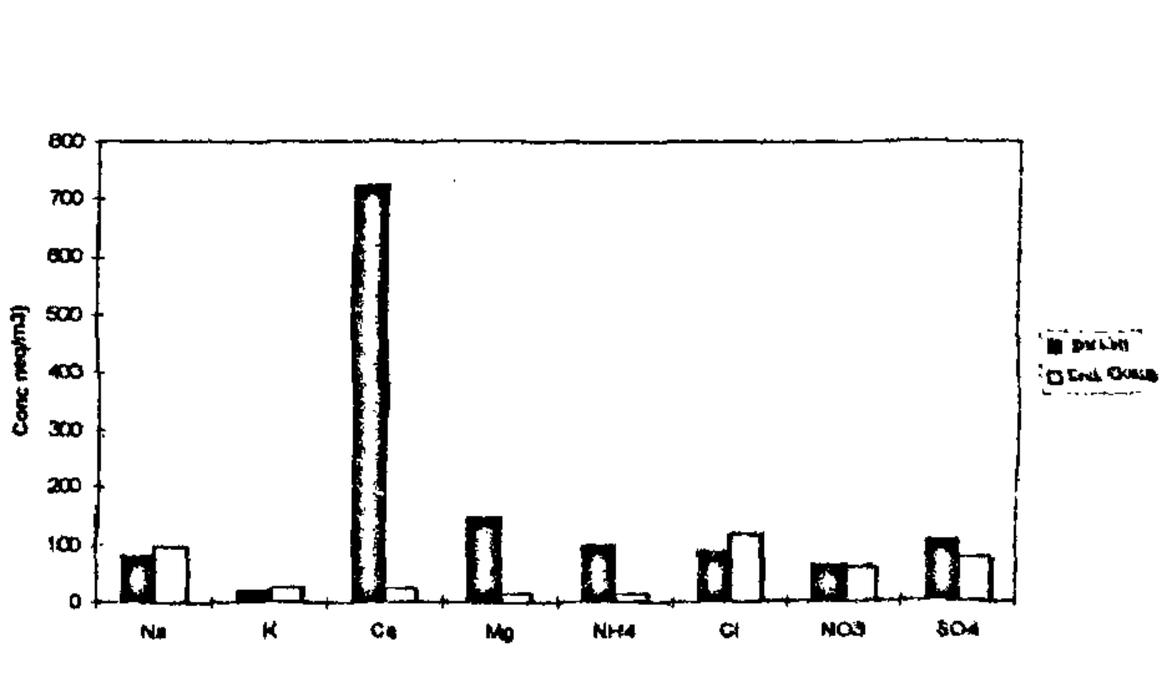

Figure 7. Concentration of water soluble components of TSP at Delhi and over Indian Ocean.

Table 1. Sea salt ratios in rainwater

	SK109	SK120	Delhi	Goa	Pune	Sea
Cl/Na	1 17	1.16	1.69	1.17	1.30	1.16
SO_4/Na	0 57	0.18	21.63	0.28	0.58	0.125
K/Na	0 027	0.036	7.85	0.07	0.04	0.0218
Ca/Na	0.162	0.07	5.70	0.43	1.08	0.0439
Mg/Na	0.31	0.25	0.62	0.25	0.47	0.227

Table 2. Percentage of non-sea salt fractions of rainwater components with respect to Na

	# 109	# 120	Delhi	Goa	Pune
SO_4	78	29.4	99	56	76
K	19.4	40	99.7	15	39
Ca	72	38	99.2	90	96
Mg	26	8	63	10	52
Cl	0.7	0.2	31	1	11

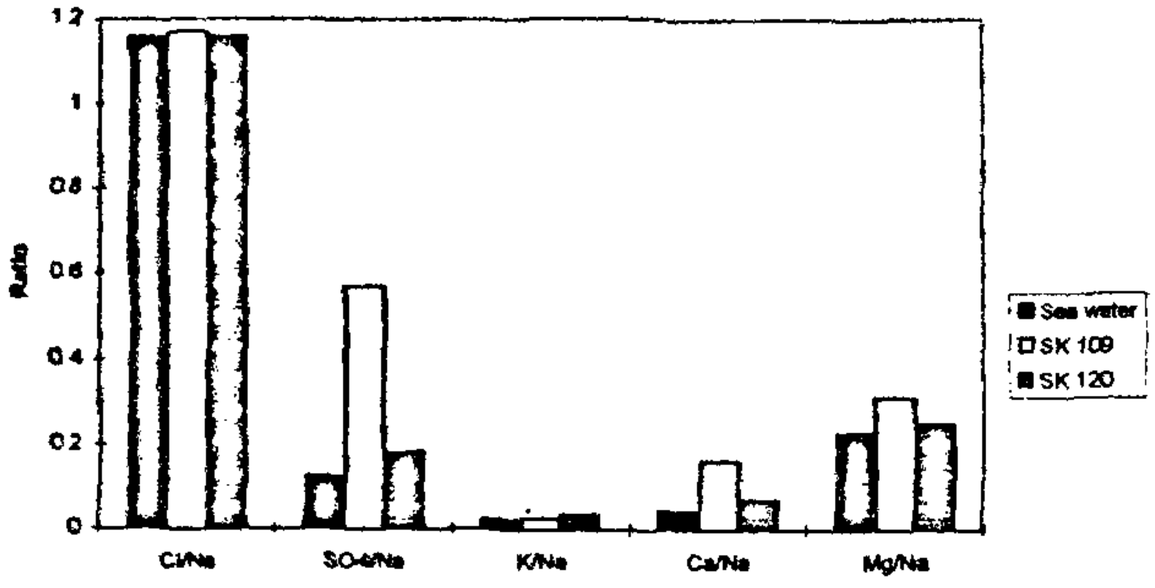

Figure 8. Sea water ratios during cruise # 109 and 120.

shows that both SO_4 and Ca ratios are very high during cruise # 109, indicating more non-marine contribution during cruise # 109 compared to cruise # 120. Figure 8 shows the sea water ratios during cruise # 109 and 120.

Table 2 presents the nss fractions (with respect to Na) in rainwater over Indian Ocean and continental sites. Other than Cl, nss fractions are very high for most of the components at all sites. Delhi has the highest nss fractions for all components. During cruise # 109, nss SO_4 is almost equal to the nss SO_4 at Pune. Similarly, nss Ca is also very high (3/4 of Pune), indicating the significant transport over the ocean from the continent.

Conclusion

Rainwater pH over the ocean is acidic ccmpared to the continental sites which may be due to excess of free acidity of sulphuric acid and lower concentrations of buffering components. Near the Indian subcontinent, the SO_4 as well as Ca were observed to be higher than over the deep ocean towards south. This indicates that N–E trade winds transport both natural and anthropogenic constituents to the ocean. The nss fractions also indicate that the transportation of crustal as well as anthropogenic constituents is significant to the ocean. It is to be further investigated why the pH of rainwater in the southern hemisphere across ITCZ is acidic. Probably, source inventory of African region may give some interesting findings.

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