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**THE ROLE OF ALKALINE PARTICULATES ON pH OF RAIN WATER AND
IMPLICATIONS FOR CONTROL OF ACID RAIN**

by

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1. Introduction

Acid rain is one of the feed back signals of man's over-grazing of his ecological niche on earth which is capable of spreading an alarm throughout his self-encapsulating cities and suburbs. Acid content of rain in many parts of the world had been steadily rising over the past several years as the countries became more industrialized and increase their use of fossil fuel. Vast areas of northern hemisphere, including central Europe, Scandinavia and northeast United States and of Canada are affected by acid rain. There is great concern that acidity of rain can have significant environmental impacts, in particular on acidification of lakes and on plant soil systems.

The main contributors to rain water acidity are sulphuric acid and nitric acid. Although no direct quantitative relationship between pollutant emissions and the measured acidity has been demonstrated, naturally and anthropogenically produced SO_x and NO_x are considered to be the major acid rain precursors. In addition to SO_x and NO_x , other pollutants may directly or indirectly affect the acidity of rain water. Ammonia, because of its alkaline nature, is able to neutralize acidic components

of precipitation. Less understood are the roles of ozone, carbon dioxide and particulate matter. Natural dust particulates, which are alkaline may be capable of neutralizing precipitation acidity.

The role of acidic particulates (SO_4 and NO_3) from anthropogenic sources on the decrease of pH values in rain water samples has been shown by many research workers in the western countries. Recently the influence of alkaline particulates on the increase of pH values has been demonstrated (Khemani et al., 1985c). The influence of alkaline dust particulates can be seen better in India where the entire area is under the influence of eolian dust blown up from the arid soils in central Asia and the Indian sub-continent, where the rain water has not yet turned acidic (Mukherjee, 1957, 1964, 1978; Handa, 1969, 1973; Handa et al., 1982; Subramanian and Saxena, 1980; Das et al., 1981; Khemani et al., 1985c); but the pollution levels are rapidly increasing. Soil in India is, by and large, dusty and rich with alkaline components like, Ca and Mg and is the major source for the observed high-levels of aerosols in the atmosphere (Khemani et al., 1985a). The concentrations of total suspended

particulates (TSP) reported for big cities in India have varied between 200 and 800 $\mu\text{g m}^{-3}$ (NEERI, 1980).

In order to examine the influence of soil dust on pH of rain, chemical composition of rain water samples and TSP have been undertaken at a few locations in India comprised of urban and non-urban regions.

2. Observational Sites

The locations where observations have been made are shown in Figure 2.1. Environmental conditions of the locations are described below.

Figure 2.1

2.1 Delhi ($28^{\circ} 35'$ N, $77^{\circ} 12'$ E, 218 m asl).

Delhi, an urban environmental station, is situated about 1100 km away from the nearest coast on the north Arabian sea. Delhi region is located in the border zone lying between the rich rain-washed Gangetic plains to the east and the semi-arid tracts of Rajasthan to the west and southwest. Being the capital of India, its air pollution problems have attracted much attention from the environmental scientists.

The rain water samples have been collected during ¹¹⁶monsoon season⁵ (July-September) of 1963 and 1984. The TSP samples have been collected in the afternoons from 1100 to 1500 hours IST, when the convective activity was maximum. Altogether, 116 TSP samples have been collected between February and October 1980. The TSP and rain water samples have been collected from the terrace of the Institute's building (a field station of the Institute), situated on a ridge, at a height of about 15 m above ground level. The samples obtained from the above location are representative of natural conditions, since the observational site is generally free from obstructions and sources of local pollution.

2.2 Agra ($27^{\circ} 10'N$, $78^{\circ} 02' E$, 169 m asl)

World famous monument Taj Mahal is situated at Agra which is about 100 km away from Delhi. There are no major industrial complexes located in the vicinity. The Mathura refinery^e has started functioning only in 1980. The rain water samples have been collected during southwest monsoon (July to September) in 1963 and 1984.

2.3 Pune ($18^{\circ} 32'N$, $73^{\circ} 51'E$, 559 m asl)

Pune is also an urban environmental station and is about

100 km away from the west coast of India. It is located on the leese side of the Western Ghats. The airflow in the lower troposphere is predominantly westerly during southwest monsoon (June-September). A large influx of ~~the~~² moisture is brought inland from the Arabian sea. The wind in the lower troposphere reverses with the withdrawal of the monsoon and the easterly flow sets in from October. The continental air masses, rich in nuclei of continental origin, pass over the region during that period.

The rain water samples have been collected during monsoon season (June-September) for a period of ten years from 1974 to 1983. The TSP samples have been collected during afternoon from 1100 to 1500 hrs IST for a period of one year from May 1977 to April 1978. The TSP and rain water samples have been collected on the terrace of the Institute's building at a height of 12 m above ground level. The samples obtained from the above locations are representative of natural conditions since the observational site is free from obstructions and sources of local pollution.

2.4 Sinhagad ($18^{\circ} 21'N$, $73^{\circ} 45'E$, 1315 m asl)

Sinhagad is a non-urban environmental hill station and is located about 18 km southwest of Pune city. It is in the forest-dense region of Maharashtra state and is sparsely populated. Daily two samples of TSP, each for 4-hour duration, have been collected in morning (0600-1000) and night (1800-2200) hours for a period of 6 days during January 1982.

2.5 Sirur ($18^{\circ} 50'N$, $74^{\circ} 23'E$, 582 m asl).

Sirur is a non-urban station and is about 130 km away from the west coast of India and is situated on the leeseide of the Western Ghats. This region is known as rain-shadow area of Deccan Plateau. The west to east orography from coast of Bombay is a rise of surface which ends in a plateau of the average height of 0.6 km. The Western Ghats (range of hills) extend from north to south along the west coast. The rainfall during southwest monsoon period on the windward side of the Western Ghats is strongly orographic. The precipitation increases with altitude from the coast of the windward side and falls off sharply on the leeseide. The average rainfall during monsoon period is less than 40 cm at the observational site. The rain

water samples have been collected during four monsoon seasons from 1979 to 1982.

2.6 Raichur ($16^{\circ} 12'N$, $77^{\circ} 21'E$, 389.5 m asl).

Raichur is also a non-urban environmental station. It is situated well inland and is free from industrial pollution. Daily two samples of TSP, each of 3-hour duration, have been collected from the terrace of the agricultural college building at a height of 10 m above ground level, in the morning and evening hours for a period of 12 days during February 1980. The TSP samples collected from the above site are representative of the natural conditions since the observational site is completely free from local pollution.

2.7 Tuticorin ($8^{\circ} 45'N$, $78^{\circ} 11' E$, 4 m asl)

Tuticorin is a coastal environmental station and is situated on the east coast of India in gulf of Mannar. There is no major industry located in the vicinity of the observational site except petrochemical industry which manufactures fertilizers. The Tuticorin thermal power plant of 620 MW capacity was under construction at the time of measurements. Daily two samples of TSP have been collected in the upwind and downwind of the

power plant from the terrace of residential building at a height of 10 m above ground level in the morning and evening hours for a period of 10 days in February 1978.

2.8 Sarni ($22^{\circ} 07'N$, $78^{\circ} 10' E$, 436 m asl).

Sarni is a thermal power plant environmental station and is located well inland in the forest area of Madhya Pradesh State of India. A 722.5 MW thermal power plant has been operating at this place without electrostatic precipitators. Daily three samples of TSP of 3-hour duration have been collected in the upwind and downwind of the thermal power plant in the morning, afternoon and evening hours for a period of 10-days during May 1982.

2.9 Sea areas

Observations over the sea areas around the Indian sub-continent have been made on board the research vessel ' Gaveshani ' of the National Institute of Oceanography, Panjim, Goa. The cruise of the ship is shown in Figure 2.2. Three samples of TSP of 3-hour duration have been taken daily during morning, afternoon and evening hours for a period of 12 days during May 1983.

Figure 2.2

The sampling equipment has been mounted on the upper deck on the upwind side of the ship to avoid ship's exhaust and on-board dust. The sampling level has been about 10 m above sea water level and care has been taken to avoid any direct sea spray contamination.

2.10 Bombay region

80% of the industries in the Maharashtra State of India are located in the Bombay region. Majority of the industries are situated in the Chembur area which is highly industrialized area throughout the India. The locations of the places where rain water samples have been collected are shown by symbol cross-upon-circle in Figure 2.3. These are Alibag and Colaba which are situated on the west coast and Kalyan which is situated eastward. The areas where major industrial establishments, such as refineries, petrochemical complexes, cotton mills, textile factories, synthetic material plants, thermal power stations have been situated are shown marked by solid stripes in the figure. Alibag is about 30 km away from Colaba and is free from industrial pollution (Khemani et al., 1980). Colaba

which is located on the south western tip of the urban industrial complexes, is, no doubt, in the upwind side of the pollution sources. But, being situated in the immediate vicinity of some of the pollution sources, it may not be free from the influence of the pollution sources. Kalyan is surrounded by industrial complexes and is affected by pollution sources of various kinds.

Figure 2.3

Weekly rain water samples have been collected simultaneously at Alibag, Colaba and Kalyan during southwest monsoon season of 1974.

3. Sampling and Analysis

The total suspended particulates (atmospheric aerosols) have been collected on Whatman 41 filter paper (10 cm dia) using a high volume air sampler (Staplex, U.S.A.) at a flow rate of $0.6 \text{ m}^3 \text{ min}^{-1}$. Whatman filter paper was chosen for its strength to withstand relatively high air-flow rates. Also, this filter paper has adequate capacity to trap small particles with high efficiency and is known for its elemental purity (Dams et al., 1972). Each sample has been extracted separately by a Soxhlet extractor for chemical analysis of water soluble

components of TSP by standard extraction methods. The water soluble extracts have been analysed for Cl , SO_4 , NO_3 , NH_4 , Na , K , Ca and Mg .

The rain water samples at a few locations mentioned in Section 2, have been collected using stainless steel funnels of 30 cm dia fitted on to 1 litre capacity polythelene bottles previously rinsed with deionized water. The funnels are washed twice daily during morning and evening to avoid dry deposition. However, contamination due to dry deposition cannot be completely ruled out. During the southwest monsoon period of 1983, rain water samples have been collected on 4 occasions on board DC-3 aircraft with the help of a stainless steel scoop fabricated for the purpose. Details of the collection from aircraft have been reported (Khemani et al., 1982a). All the rain water samples are filtered through Whatman 41 filter papers and refrigerated at 4°C in the laboratory until all the ionic components are analysed. The samples have been analysed for the ionic components Cl , SO_4 , NO_3 , NH_4 , Na , K , Ca and Mg . Also, the pH values have been determined in all the samples collected. The chemical composition of rain water at Chembur, a highly industrialized location at Bombay, is reported (Sequeira, 1976), and

these values in the present study are referred to for comparison.

The concentrations of Cl , SO_4 , NO_3 and NH_4 have been determined using standard colorimetric methods (Khemani et al., 1985c). The concentrations of metallic components have been determined by Kipp and Zonen flame photometer up to 1978 and by double beam atomic absorption spectrophotometer (Perkin-Elmer, Model 373) with air-acetylene flame, subsequently. The calibration curves for different chemical constituents have been obtained by preparing standard solutions using grade chemicals. These calibrations were periodically repeated to check accuracy. The concentrations of different chemical constituents have been obtained with reference to the blank solutions. The analytical errors are nominal and vary within $\pm 10\%$

The pH has been measured with a pH meter using reference (KCl) and glass electrodes standardized with pH 4.0 and pH 9.2 reference buffers before and after pH determinations. Hydrogen ion concentration has been deduced from the measured pH. Since pH value is influenced by extreme values of rainfall amount, rainfall weighted mean values of pH have been used instead of arithmetic means.

4. Concept of pH Value

The reference level commonly used to compare acid precipitation to natural precipitation is pH 5.6, the pH that results from the equilibration of atmospheric CO_2 with precipitation. This reference level has been chosen because of the ubiquity of CO_2 in the global atmosphere and because of the absence of data on other acids or bases. However, Galloway et al., (1982) believed that there was no single natural pH of precipitation applicable to the whole globe, but rather several natural values, each unique to a region, the size of a continent or an ocean. From the measurements of pH values in rain water collected at five remote areas of the globe, they suggested that the lower limit of natural pH was probably ≥ 5 . However this lower limit of natural pH cannot be applicable in the Indian sub-continent where the pH values are highly alkaline and vary from 6.0 to 7.5 (WMO, 1984). These values are much above the CO_2 - equilibrated pH. The pH values in Central Europe are around 4 and this value increases towards the oceans and also towards eastern Europe (Georgii, 1982). Over the north American Continent, high-pH values have been observed over the middle and western part of the United States. Only at the east coast the acidity of the rain

leads to pH 4.5. The pH data in the present study are interpreted in the light of the CO_2 - equilibrated value (pH = 5.65) observed in the laboratory, though it may not be well suited for real atmospheric background value.

5. Southwest Monsoon

An important weather system which has been largely neglected for study of its chemical character, is the south Asian summer monsoon. The southwest monsoon sets in over the extreme southwest coast of India in late May and by the first week of July it is established over the entire country. The monsoon current reaching India has had a fairly long journey (6500 km) over ocean. Under the influence of strong and persistent surface winds blowing over and from the Arabian sea, vast quantities of airborne sea salt are expected to be transported into the country over a considerable part of the year (Eriksson, 1959, 1960). Giant and large sea salt nuclei carried by the monsoon air flow are known to penetrate deep inland as far as up to Delhi in north India (Kapoor and Ramana Murty, 1966). The monsoon weakens by September and by middle of October withdraws from the entire country.

6. Results and Discussion

6.1 Chemical composition of rain water

The average seasonal concentrations of major ionic components along with pH values in rain water collected simultaneously during 1974 at the 5 stations, Alibag, Colaba, Kalyan, Chembur and Pune, are given in Table 6.1. The seasonal variations of ionic components in rain water collected at Pune for a period of a decade from 1974, are shown in Figure 6.1. The average seasonal concentrations of ionic components along pH values in rain water collected at non-urban station Sirur for a period of four years from 1979 are given in Table 6.2. Also, the average seasonal concentrations of major ionic components along with pH values, in rain water samples collected at Delhi during 1965 and 1984 and at Agra during 1963 and 1984, are given in Table 6.3.

Tables 6.1, 6.2 and 6.3. Figure 6.1

(a) Chloride and Sodium

The maximum concentration of Cl has been observed at Alibag, a non-urban coastal station and minimum at Pune (Table 6.1), an inland station on the leeward side of the

Western Ghats. The variation of Na is similar to that of Cl. It is known that the concentration of sea salt (Cl and Na) decreases with an increase of distance from the sea. Chloride and sodium at Pune have varied from 1.03 and 0.82 mg L⁻¹ in 1975 to 2.57 and 1.84 mg L⁻¹ respectively (Figure 6.1). At Sirur, concentration of Cl has varied from 2.03 mg L⁻¹ in 1979 to 3.85 mg L⁻¹ in 1981, and the concentration of Na has varied from 1.02 mg L⁻¹ in 1980 to 2.87 mg L⁻¹ in 1981 (Table 6.2). The concentrations of Cl and Na have not shown much variations during the two monsoon periods at Delhi and Agra (Table 6.3).

The predominant source of Cl in rain water is sea spray. A small amount of Cl is also contributed by anthropogenic emissions i.e., hydrochloric acid. Data on the latter are sparse but it is known that the anthropogenic emissions are negligible compared to the natural ones. It is, therefore, assumed that Cl does not indicate an addition of acid or base in rain water (Granat, 1972). Sodium in rain water at coastal stations is mainly derived from sea spray, whereas at inland stations soil has been considered to contribute some portion of Na in rain water. A significant positive correlation ($r = 0.96$) has been observed between Cl and Na at all the

stations in the Bombay and Pune regions and also at Agra and Delhi suggesting that Cl and Na are having common source which is the sea. The sea salt (Cl and Na) has been considered neutral salt and the presence of it does not influence the pH in rain water (Granat, 1972).

(b) Sulphate

The maximum concentration of 20.2 mg L^{-1} has been reported at Chembur, a highly industrialised location in the Bombay region and the minimum (1.11 mg L^{-1}) has been observed at Alibag. Although Colaba is situated in the west coast, the concentration of SO_4 (2.58 mg L^{-1}) at Colaba is twice of that at Alibag. This could be due to the proximity of Colaba to the industrial complexes. Low concentration of SO_4 at Alibag indicates that the station is free from industrial pollution. The second maximum concentration has been observed at Kalyan (5.20 mg L^{-1}) which is also situated in the industrial complex area.

The concentration of SO_4 at Pune has varied from 0.42 mg L^{-1} in 1982 to 2.39 mg L^{-1} in 1975. Sulphate concentration at non-urban station Sirur, has varied between 0.90 and 2.77 mg L^{-1}

during the four monsoon seasons. The concentrations of SO_4 at Delhi and Agra increased by 120 and 37% respectively after a period of two decades when the cities became more industrialized (Table 6.3).

Sulphate in rain water arises mainly from anthropogenic emissions which is also indicated by the above observations. The sulphate from sea spray is neutral and does not increase the acidity of rain water (Granat, 1972). However, SO_4 from anthropogenic sources has been considered a major component which increases the H ion concentration in rain water and decreases its pH (Nagamoto et al., 1983). In order to find out the effect of anthropogenic SO_4 at the coastal stations, it is essential to eliminate the contribution by sea spray. Assuming that all Na is of sea-origin, the contribution by sea to the observed values of SO_4 are calculated. The contribution of SO_4 by sea spray is maximum (86%) at Alibag, non-urban coastal station. The contribution by sea decreases to 30% at Colaba which is located in the proximity of the industrial complexes. However, the contribution by sea in the industrial complex at Chembur and Kalyan is minimum (3 and 11%). The contribution by sea at Pune, a station

relatively free from industrial pollution is around 20%.

(c) Nitrate

The concentration of NO_3 is minimum at coastal stations Colaba (0.40 mg L^{-1}) and Alibag (0.57 mg L^{-1}) which are free from industrial pollution. However, maximum concentration (5.14 mg L^{-1}) has been observed at Sirur, an inland non-urban station. The concentration of NO_3 at Pune varied from 0.45 mg L^{-1} in 1977 to 1.34 mg L^{-1} in 1975. The concentration of NO_3 has been observed, by and large, same at Delhi and Agra (Table 6.3).

Soil seems to be a major source of nitrate in India, Maximum concentration of NO_3 in rain water at Sirur, pollution free non-urban station, indicates that soil is the source of NO_3 . Also, NO_3 showed significant correlation with soil-oriented components at Sirur (Naik, 1985).

Nitrogen oxides are emitted into the atmosphere mainly through the action of bacteria in the ground but also through oxidation of nitrogen by combustion (Green, 1972; Cox, 1974; Penkett et al., 1979). NO and NO_2 will eventually end up as NO_3 in rain water through various reactions. Thus the HNO_3 formed

in rain water can increase the H ion concentrations. But it has been observed at Pune that during monsoon season sea salt ($NaCl$) reacts with HNO_3 and results ⁱⁿ the formation of $NaNO_3$ particles (Khemani et al., 1982b). This reaction will be in position to neutralize the acidic effects of HNO_3 and helps in reducing the extent of H ion concentration in rain water. Probably due to this reason, the NO_3 in rain water at Pune has not shown significant correlation with pH (Khemani et al., 1985c). Also, at Delhi and Agra, NO_3 has shown significant correlation with soil-oriented components (K and Ca). Hence NO_3 in rain water in India does not seem to influence the pH values.

(d) Ammonium

Maximum value has been observed at Chembur (2.10 mg L^{-1}) and minimum value at Alibag (0.27 mg L^{-1}) in the Bombay region. At Pune it has varied from 0.10 mg L^{-1} in 1981 to 0.80 in 1975. Minimum concentration has been observed at non-urban station, Sirur where the concentration has varied between 0.04 to 0.14 mg L^{-1}). At Delhi the concentration was 0.23 mg L^{-1} during 1965 and the value became more than twice ^{this} in 1984. However at Agra, the concentration has been 0.20 in 1963 and a little high ^{or} during

1984 (0.33 mg L^{-1}).

Ammonium in precipitation emanates from ammonia created by the action of bacteria on nitrogen compounds in the ground, perhaps mainly from urine (Healy et al., 1970). It is also released from the industrial plants manufacturing fertilizers. The presence of NH_4 in rain water helps in neutralising the acidic effects caused due to presence of SO_4 in the form of H_2SO_4 . It has been found at Pune that most of sulphates during monsoon season are in the molecular form of ammonium sulphate (Khemani et al., 1982b) and the presence of such particles could reduce the extent of H ion concentration in rain water.

(e) Potassium, Calcium and Magnesium

The concentration of K has varied from 0.88 mg L^{-1} to 1.13 mg L^{-1} in rain water in the Bombay region. At Pune it has varied from 0.11 mg L^{-1} in 1982 to 0.53 mg L^{-1} in 1974. At Sirur it has varied from 0.43 mg L^{-1} to 1.25 mg L^{-1} during the four monsoon seasons. At Delhi it has been 0.42 mg L^{-1} during 1965 and increased three times after a period of about two decades in 1984. At Agra the concentration has been 2.00 mg L^{-1} during 1963 and remained, by and large, ^{the} same after a period of [^]

two decades in 1984.

The concentration of Ca has varied from 1.86 mg L^{-1} to 2.56 mg L^{-1} in the Bombay region. At Pune it has varied from 1.15 mg L^{-1} in 1979 to 2.17 mg L^{-1} in 1977. At Sirur it has varied from 1.46 mg L^{-1} in 1979 to 6.51 mg L^{-1} in 1982. At Delhi it has been 4.83 mg L^{-1} in 1965 and reduced to nearly half (2.95 mg L^{-1}) after period of two decades in 1984. Similarly at Agra, the concentration has been 9.36 mg L^{-1} in 1963 which has been reduced to half after a period of two decades in 1984.

The concentration of Mg has varied from 0.47 mg L^{-1} to 0.6 mg L^{-1} in the Bombay region. At Pune it has varied from 0.23 mg L^{-1} in 1983 to 0.54 mg L^{-1} in 1977. At Sirur it has varied from 0.37 mg L^{-1} to 1.46 mg L^{-1} . The concentration at Delhi has been 0.62 mg L^{-1} and at Agra it has been by and large, similar to that at Delhi.

Compounds containing K, Ca and Mg are added into the atmosphere by soil erosion, sea spray and by anthropogenic emissions. It has been considered that these soil-oriented elements are mostly in the form of carbonates (Granat, 1972).

Examples of anthropogenic emissions of K, Ca and Mg are fly ash from burning of coal or oil and exhausts from processing industries. For urban areas anthropogenic emissions are of importance, whereas for the other places soil is the major contributor.

These elements are potentially basic in nature and their presence in high concentration in rain water helps in neutralising the acidic effects of anthropogenic emissions (SO_4 and NO_3) and maintain the pH of rain water in alkaline range.

6.2 Ratio of Major Components to Sodium

The ratio values of major sea salt components to sodium are remarkably constant in the oceans and seas of the world with exception of coastal and land-locked seas (Horne, 1969, Riley and Chester, 1971). However, the values in marine aerosol and precipitation have on occasions been observed to be different from their corresponding values in sea water (Junge, 1972, Tsunogai et al., 1972). The effects of soil dust, originating from the arid zones of continents, on the chemical composition of aerosol particles over the ocean atmosphere have been observed (Prospero and Carlson, 1972, Prospero and Nees, 1977; Junge, 1979; Prospero et al., 1981; Hirose et al., 1983; Khemani et al., 1985b).

(a) Cl/Na and Mg/Na

The ratio values for all the major chemical components with respect to Na for the seven stations are given in Table 6.4. Chloride in rain water is usually thought to be mostly from the sea, like Na and Mg and the ratio of Cl/Na at the coastal stations (Alibag, Colaba and Kalyan) as well as at the inland stations (Pune, Sirur, Delhi and Agra) are found to be less than in sea water. Many comments on the ratio can be found in literature; about smaller ratios due to loss of Cl and/or addition of Na from continental sources. The ratio, Mg/Na, at Alibag (0.16) is closer to that of sea water (0.13) than at other stations. There is strong correlation ($r = 0.96$) between Cl and Na and Cl and Mg ($r = 0.67$), suggesting that Cl, Na and Mg are intimately related and originate predominantly from the sea which is consistent.

Table 6.4

(b) K/Na and Ca/Na

The ratio K/Na at all the stations is higher (0.23 to 0.79) than in sea water (0.036). The excess of K in rain water is attributable to the local use of K-containing fertilizers in agriculture and the wide spread use of firewood as a domestic fuel.

The ratio of Ca/Na is significantly ^{higher} ~~more~~ not only at the inland station Agra (3.14) but also at the coastal stations (0.62 - 0.82) than in sea water (0.038). Excess Ca in rain water has been reported for coastal as well as for inland stations in India (Ramachandra Murty and Ramana Murty, 1969; Khemani, 1974; Sequeira, 1976; Sadasivan, 1977; Sequeira and Kelkar, 1978; Khemani et al., 1985c). Excess of Ca, therefore, is a regular feature of monsoonal precipitation. The excess of Ca concentration of 1.1 mg L^{-1} is uniformly distributed over the country (Sequeira and Kelkar, 1978). Due to mixing of maritime and continental air masses in the eastern Arabian sea (Rao and Desai, 1973), it is considered that Ca from soil dust is incorporated into Indian rains. Calcium in rain water samples, is present in the form of CaCO_3 (Sequeira and Kelkar, 1978). Excess Ca has been observed in marine aerosols over the west coast of India, which has been attributed to the transport of soil dust from the Arabian peninsula towards the west coast of India (Khemani et al., 1985b).

(c) SO_4/Na

The ratio of SO_4/Na is higher than sea water at all the

stations, except at Alibag (0.29) where it is ^{close} ~~neaper~~ to the sea water ^{value} (0.25). The excess has been found minimum (14%) at the coastal station Alibag. It has been found that the excess SO_4 in the marine aerosols over the sea areas around Indian sub-continent is about $0.21 \mu\text{g m}^{-3}$ and its contribution is around 20% (Khemani et al., 1985b). Whereas, the average concentration of excess SO_4 in the marine aerosols over the north Atlantic is about $0.9 \mu\text{g m}^{-3}$ and its contribution has varied from 60 to 80% (Gravenhorst, 1978). This feature indicates that air around India is quite clean and its sea regions can serve suitable sites for the study of background pollution in the northern hemisphere.

6.3 Wet Deposition of Ionic Components

The wet deposition in mg m^{-2} of the ionic components have been computed by multiplying the total monthly precipitation by the measured weighted mean concentrations of ionic components. The monthly values are added and the seasonal depositions thus obtained for the 3 stations in the Bombay region are given in Table 6.5. The seasonal depositions of ionic components for Pune have been computed for the ten year period (1974-1983) and

the results are shown plotted in the form of histograms in Figure 6.1.

Table 6.5 and Figure 6.1

The sea salt (Cl and Na) deposition is maximum at the coastal stations Alibag (13504, 8686 mg m^{-2}) and Colaba (9609, 7242 mg m^{-2}) which is consistent. The deposition from anthropogenic sources (SO_4) is higher at Colaba (5988 mg m^{-2}) than at Alibag (2511 mg m^{-2}). At Kalyan the deposition of SO_4 (9570 mg m^{-2}) has been found maximum. The total deposition at Pune has been maximum in the case of SO_4 (10148 mg m^{-2}) followed by Cl (9686 mg m^{-3}) and Ca (8923 mg m^{-2}).

Apart from the sea salt which is neutral and does not therefore influence the pH of rain water, the other ionic components which are present in substantial amounts are SO_4 and Ca. The dominance of these components in rain water influence the pH to a greater extent.

6.4 pH of Rain Water

The various aspects contributing to the formation of acid precipitation have been discussed by many investigators. Junge and Scheich (1969) have found that particles of smallest size

range, sampled in rural areas, reacted acid whereas the coarse fraction reacted more alkaline. This tendency has also been found to be valid for marine aerosols present 15 m above the north Atlantic (Gravenhorst, 1975), and in the Arctic (Winkler, 1980). The coarse particles, which are also called primary aerosols, are formed by sea bubbling or blown up frequently from basic mineral soil whereas, the smallest particles (secondary aerosols) are formed by gas-to-particle conversions leading to acidic nuclei. Hence, the relative contribution of primary aerosols (Ca, K and Mg) and secondary aerosols (SO_4 and NO_3) in rain water will decide the pH of rain water.

The pH of rain water at the different stations are included, as mentioned earlier, in Tables 6.1, 6.2 and 6.3. The values at Alibag and Colaba have been 7.2 and 7.1 respectively which are in the highly alkaline range. The value at Kalyan has been 5.7 which is nearer to the neutral value of distilled water. However, at Chembur the pH value has been reported 4.8 which is acidic. At Pune, the pH value has varied from 6.1 in 1983 to 6.8 in 1977 indicating that rain water at Pune is not acidic. At Sirur, the pH values have varied between

6.4 and 7.4 which is in alkaline range. At Delhi, the pH value was alkaline (7.0) in 1965 and remained alkaline (6.1) after the period of about two decades in 1984. At Agra, the pH value was 9.1 during 1963 which is highly alkaline. After a period of about two decades the pH has decreased by 2.8 units but still lie in the alkaline range (pH = 6.3).

The correlations (r) worked out between pH and different ionic components from long series of rain water data at Pune, are given in table 6.6. Significant positive correlation ($r = 0.56$) has been noticed only with calcium suggesting that it is this ionic component which has influence on the observed pH of rain water. Khemani et al., (1985c) have shown inverse relationship between hydrogen ion concentration and excess cations (Ca, K and Mg) in the rain water samples at Pune. They suggested that the excess cations in rain water are responsible for the observed alkaline pH values.

Table 6.6

Sulphate and Calcium are the dominating ionic components present in rain water in India. To illustrate the relationship of hydrogen ion concentration with Ca and SO_4 , the data obtained for the rainy day during July 1965 at Delhi has been

considered. Seventeen samples were collected in a shower which lasted for two and half hours on 31 July 1965. The variations in the concentrations of Ca and SO_4 along with Hydrogen ion is shown plotted in Figure 6.2. No significant relationship has been noticed between SO_4 and H ion indicating that some of SO_4 might be present in the form of salts. A weak correlation ($r = 0.36$) has been observed between SO_4 and H ion concentration. But Calcium has shown significant ($r = 0.65$) anti-phase relationship with H ion, indicating that this basic component reduces H ion in rain water rendering it alkaline. Similar results have been found in rain water samples collected at Pune (Khemani et al, 1985). Soil is considered to be the main source of Ca and industrial pollution the main source of SO_4 particles in the atmosphere. The presence of these two components influences the pH of rain water as already pointed out.

This feature is further examined by calculating anion-cation balance of the rain water collected during monsoon period of 1974 at five stations, Alibag, Colaba, Kalyan, Pune and Chembur (Table 6.7).

Table 6.7

The anion sum includes Cl , SO_4 and NO_3 , while the cation sum includes NH_4 , Na , K , Ca and Mg . Examination of the values of anions and cations indicates that cations are in excess at all the stations except at Chembur, a highly industrialized location, where the rain has been reported acidic ($\text{pH} = 4.8$). The main cause for alkaline rain is the presence of high concentration of Ca and other soil-oriented elements which are alkaline in nature and neutralize the acidic effects generated by the presence of SO_4 and NO_3 . However, the cause of acidic rain at Chembur is the presence of very high concentration of SO_4 (20.2 mg L^{-1}) which could not be neutralised by the available Calcium (3.1 mg L^{-1}) and other alkaline elements. Nature has played its role in keeping the rain water in alkaline range in Bombay (Sequeira, 1976) inspite of acidic nature of rain in a limited zone of two square kilometer at Chembur. High concentration of Ca in rain water samples in Bombay has been attributed to the soil dust transported from the Arabian peninsula towards west coast of India (Khemani et al., 1985b). The alkaline elements in the soil dust play an important role in rainout and washout processes during monsoon season and neutralises the acidic effects of pollutants released from the

industrial complexes. It is to be noted that Bombay region receives heavy rainfall during the southwest monsoon season.

The influence of alkaline particulates from soil dust on the pH of rain water has been reported in the United States and European countries. The analysis of rain water data for 1953-54 and for 1977-78 reported from the northeast United States (Stensland and Semonin, 1982), showed that the rain water in that region became acidic because of the deficiencies of alkaline components like Ca and Mg which were significantly less in the years 1977-78 than in the years 1953-54. Peters et al., (1982) reported an increase of H ion concentration in the 13 years precipitation data (1965-78) from nine collection sites in New York. Deficiency of soil-oriented ions (Ca and Mg) and high concentration of acidic ions (SO_4 and NO_3) were considered to be the main reasons for the increase of H ion in the rain water reported from selected sites in north America and Scandinavia (Munger, 1982). Influence of soil particulates on pH of rain water can be clearly seen from the chemical analysis of rain water samples collected at Retz, a semi-arid region in Austria. High concentration of Ca (6.06 mg L^{-1}) in rain water during 1978

has neutralised the H ion concentration to some extent and increased the pH up to 5.4 which is very near to the boundary value of rain acidity (Cihak and Chalupa, 1985). Rain water at Retz, like India, could have been in the alkaline range, but high concentration of SO_4 ($\sim 17 \text{ mg L}^{-1}$) transported from the industrial sources in Europe has over powered the natural source and maintained the pH towards acidic range.

Hence the main cause for alkaline rain water in India is the presence of high concentration of alkaline aerosols (cations) dispersed from dusty soil and transported in the atmosphere, which are washed out by precipitation. The above influence is supported by the high pH value, in rain water reported from 10 background monitoring stations in India (WMO, 1984). Mukherjee et al., (1981) have suggested another cause for higher alkaline pH values, close to 7.0 in precipitation in India. They have shown that higher atmospheric temperatures in tropics, lower solubility and dissolution rates of carbon dioxide added with rapid process of cloud formation and precipitation result in higher pH values. Also, greater depth of saturated air during southwest monsoon period may be another factor for higher pH.

6.5 Influence of Power Plant on pH of Rain water

During the field observational programme on the measurements of gaseous and particulate pollutants around thermal power plant at Sarni in May 1982, one rain water sample was collected which showed pH 6.8. Alkaline pH has been attributed to the washout effect of giant particles of fly ash released from the stacks of the power plant which is operating without electrostatic precipitators. Also, the lake water collected in the downwind of power plant showed highly alkaline pH (8.2) which is due to the deposition ^{of} large amount of giant particles of fly ash in the lake. It has been considered that alkaline fly ash emissions are capable of neutralizing precipitation acidity.

The above feature is corroborated by the reported alkaline pH value (7.4) in the rain water samples collected at the site of another thermal power plant, located in New Delhi, which was also operating without electrostatic precipitators (Subramaniam and Saxena, 1980). It is of interest to find out what changes can occur in the pH of rain water if the particulates from the stacks of the power plant are allowed to escape along with gases. Fortunately by the end of the year 1982, this thermal power plant at New Delhi was fitted with electrostatic

precipitators and the collection of rain water samples was organized during southwest monsoon season of 1985 at the site of the plant and also in the upwind and downwind of the power plant. The samples at the site of the plant have been found acidic on 11 occasions and the pH values varied between 4.2 and 5.3. The rain water on the remaining 16 occasions have been found alkaline and the pH values varied between 5.7 and 7.8. However, the rain water samples in the upwind and downwind regions which are within the distance of 4 km from the power plant have been found alkaline and the pH values have varied between 5.7 and 8.2.

The above feature suggests that the fly ash particles are capable of neutralizing the effects of acidity in precipitation. Also, it is confirmed that acid rain, wherever it has occurred in India, is purely local phenomenon. Long-range transport of pollutants (SO_4 and NO_3) does not seem to be effective during the southwest monsoon period when the meteorological factors are favourable for quick dispersal of pollutants whose sources are weak.

6.6 Ionic Composition and pH at Cloud Base and Ground

Samples of rain water have been collected in Pune region on 4 occasions both at cloud base (1.5 km) and at ground during

southwest monsoon 1983. The values of ionic composition and pH values are given in Table 6.8. On the average, the concentrations of ionic components at ground level have ranged up to 4-times than those at cloud base level. The pH values of rain water at cloud base have varied from 5.6 to 6.1 and are lower by 1.5 units than at ground level. This observation is in conformity with what has been reported on the Island of Hawaii, namely, the pH of rain decreased with increasing altitude averaging 3.2 at sea level and 4.3 at 2.5 km (Miller and Yoshinoga, 1981). It can be seen that although pH values at cloud base are lower than those at the ground, they are in alkaline range.

Table 6.8

Examination of anion-cation balance at ground and cloud base levels pointed out that the excess cations are 3-times larger at ground level than at cloud base level. This feature suggests that excess cations (Ca and Mg) are responsible for the observed increase of pH at ground. Non-marine Mg has also been considered as a strong alkali^{ine} component with Ca which neutralizes the acidic effects in rain water. ←

Peden and Skowron (1978) have observed remarkable reduction

in H ion concentrations in precipitation samples and attributed it to the presence of particulate material in the samples. Also, Pack (1980) has reported a significant decrease in H ion concentration with event samples collected from the ERRI network due to addition of basic particulate matter. Munger(1982) has reported increase in H ion concentrations by 4-times from west to east across the northern Minnesota in USA, whereas in the same region alkaline dust (Ca and Mg) decreased by 2 to 3 times. A considerable part of H ion concentration in rain water in Hungary, is neutralized mainly by soil-derived calcium components (Horvath, 1981). Recent chemical analysis of bulk rain water samples collected at number of stations at Hungary has shown that Ca particles of soil origin play a role in the control of acidity (Horvath and Meszaros, 1984). In view of the above and in the light of the present study, it confirmed that alkaline properties of particulate matter in rain water are responsible for neutralizing the H ion concentration and consequently for the observed increase in pH.

6.7 Total Suspended Particulates (TSP)

The total acid or base potential of the material constituting the particulates is an important quantity because deposition

of particulates can either lead to deterioration or an improvement of the soil that it lands on. Most acid soils are infertile and have lost much of their nutrient ionic materials, such as Ca and K by leaching soluble salts. It is of interest, therefore, to know the acidity of TSP measured at the various locations. The calculations for sum of anions (Σ^-) and cations (Σ^+) for all the seven locations are shown in Table 6.9.

Table 6.9

The hydrogen content in the TSP has been assumed to be characterized by the difference between anions and cations ($\Sigma^- - \Sigma^+$) that is, if the difference is positive the TSP are acidic and if difference is negative the TSP are alkaline. If the principal ions have been accounted for, difference in the ion sums ($\Sigma^- - \Sigma^+$) are assigned to hydrogen ion (Hidy and Countees, 1982). The anion sum includes Cl, SO_4 and NO_3 , whereas the cation sum includes NH_4 , Na, K, Ca and Mg. Examination of the values of anions and cations in TSP (Table 6.9) indicates that the cations are more than anions at all the locations. Hence, ionic balance of TSP in different environments in India

suggests that the TSP are alkaline in nature. The main cause for the observed feature is the presence of high concentration of Ca and other soil-oriented elements (K and Mg). Calcium has been found dominant component in cations which neutralizes acidic effects generated by the presence of SO_4 and NO_3 . Most of the cations are soil-originated and their excess concentrations in the atmosphere suggest that the soil is the major source of TSP in the atmosphere over India. Most of the anions are considered to be released by anthropogenic sources (SO_4 and NO_3) and their low concentrations in TSP, suggest that pollution sources have not dominated the natural sources (soil and sea). Hence, the presence of excess cations are responsible for the absence of the acidity or hydrogen ion concentration in the aerosols in India. The deposition of such aerosols should, therefore, give rise to relatively fertile soil in India.

The effect of acidity in aerosols is observed in the pH of rain water. European rain is mostly acidic (Granat,1972b). Rain in the northeastern United States is also reported to be acidic because aerosols there are found to be acidic in nature (Hidy and Countess,1982); but rain collected in continental

sites in the United States is either neutral or slightly basic because of the large amount of dust components of the aerosols in that region (Gorham, 1976). The presence of alkaline aerosol is responsible for the alkaline pH in rain water discussed in section 6.4. This is also corroborated by the reported alkaline pH values in rain water from different parts of India (Khemani, 1985; Khemani et al., 1985c; Mukherjee et al., 1986).

In view of the above it can be generalised that the incorporation of aerosols in cloud/rain droplets depends on the hygroscopic nature and physical properties of the particles present over a region. In arid areas and under strong sea influence, precipitation should be alkaline. In areas where soil is protected against wind erosion by vegetation and where sea salt contribution is small or normal, precipitation should be acidic. These features seem to be represented in the geographical distribution of precipitation pH-values over the northern hemisphere (Gravenhorst et al., 1980; Georgii, 1982). In the arid regions of southwest United States and over the Indian sub-continent, relative high pH values ($\text{pH} > 6$) occur. The low pH values ($\text{pH} < 4$) in the northeast United States, Canada and central Europe are, however, not only the reduced alkalinity due to reduced sea and soil derived minerals in

precipitation, but also certainly include an effect related to anthropogenic acid forming emissions.

6.8 Implications of Alkaline Particulates on Control of Acid Rain.

Although the soil dust in India creates a great inconvenience to the human beings, it is a blessing in disguise. The alkaline properties of soil particulates has sustained alkaline pH in rain water so far and has been controlling acid rain in India. Defficiency of soil-oriented components (Ca and Mg) and high concentrations of acidic components (SO_4 and NO_3) have been considered to be the main causes of acid rain in the northeast United States, Europe and Scandinavian countries.

In European countries, acid rain has deteriorated the fertility of the soil which has lost much of their nutrient ionic materials such as Ca and K. Already farmers have started adding enormous quantities of lime to the soil to lower the acid content and to compensate for the loss of calcium. In the Netherlands it has been calculated that more than 20% of the lime for agriculture purpose is used in compensating for the loss of calcium by leaching of the soil by acid precipitation (Vermeulen, 1980). It appears that more quantities of

lime will be required in coming years. A Danish report has suggested that lime be added to the acidified Danish lakes to make fish and other aquatic life possible again (Vermeulen, 1980). However, the phenomenon of acid rain poses no special problem in Asia, particularly in India, so long as the aerosol state of the air, which is presently alkaline, continues to remain so.

But the problem of acid rain has become alarming in the United States and in the European countries and requires immediate attention. Rain-bearing clouds in mid-and high-latitudes can be seeded with water soluble calcium salts for the control of acidity in rain water. Another alternative solution to the problem of acid rain lies in the decrease in emission of sulphur and nitrogen oxides to the atmosphere. This objective can be achieved with the combination of improved control technology and the conservation of fuel.

7. Conclusions

The study of chemical composition of rain water and total suspended particulates at a few places in India has shown that concentrations of acidic components (SO_4 and NO_3) from the

industrial sources are minimum as compared to alkaline components (Ca, Mg and K) which are released from the soil. Apart from sea salt, SO_4 and Ca have been found to be the dominant components in rain water.

The pH values of rain water at different locations have been found much above the CO_2 -equilibrated value and the pH values have mainly varied between 6 and 9.

The correlations (r) worked out between pH and different ionic components from the long series of rain water data at Pune, have shown that out of all the ionic components, only Ca has been found significantly correlated with pH. Hydrogen ion concentration has shown an inverse trend of variation with excess cations. This feature suggests that excess cations which are alkaline in nature, are mainly responsible for the observed alkaline pH. Low pH values in rain water in India, are restricted to localized regions in highly industrialized cities like Chembur in Bombay from where acid rain has been reported.

Acid rain has been observed during the monsoon season of 1985 at the site of thermal power plant when it was operating with electrostatic precipitators. Before the installation of

electrostatic precipitators the rain water samples collected at the site of the plant have been reported highly alkaline. However, the rain water samples collected within the distance of 4 km during 1985 in the upwind and downwind regions have shown alkaline pH. This feature indicates that long-range transport of pollutants does not seem to be effective in tropical country like India during southwest monsoon period when the meteorological factors are favourable for quick dispersal of pollutants whose sources are weak.

The pH values in rain water at Agra and Delhi during 1963 and 1965 respectively were in alkaline range and remained in that range even after a period of two decades when the cities developed industrially to a great extent.

A comparison of chemical composition and pH of rain water at cloud base with that at ground level has shown that the concentrations of cations decrease up to 4-fold from ground level to cloud base level. The pH values of rain water at cloud base level have varied from 5.6 to 6.1 and are lower by 1.5 units than the values at ground level. This feature suggests that increase in cations, especially Ca, is responsible for

the observed increase of pH at the ground.

The cations exceed the anions in the aerosols at the different locations studied. This result indicates that the aerosols are potentially basic in nature in India and are capable to render the pH of rain water alkaline.

The concentrations of soil-oriented components (Ca, K and Mg) in the atmospheric aerosols have been found higher and that of acidic components (SO_4 and NO_3) lower than those reported for the western countries which are industrially much more developed. Hence, the alkaline properties of soil and fly ash particulates have sustained high alkaline pH in rain water and have been controlling acid rain in India. Defficiency of soil-oriented components (Ca and Mg) and high concentrations of acidic components in rain water are the main causes of acid rain in the northeast United States, Europe and Scandinavian countries.

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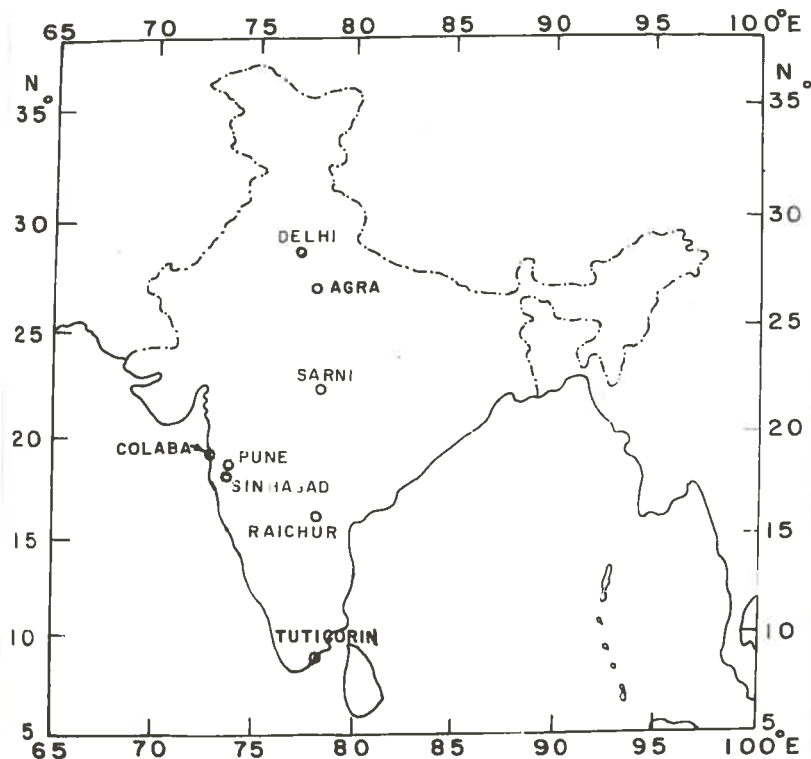


Figure 2.1 Map of India showing the locations of observational sites.

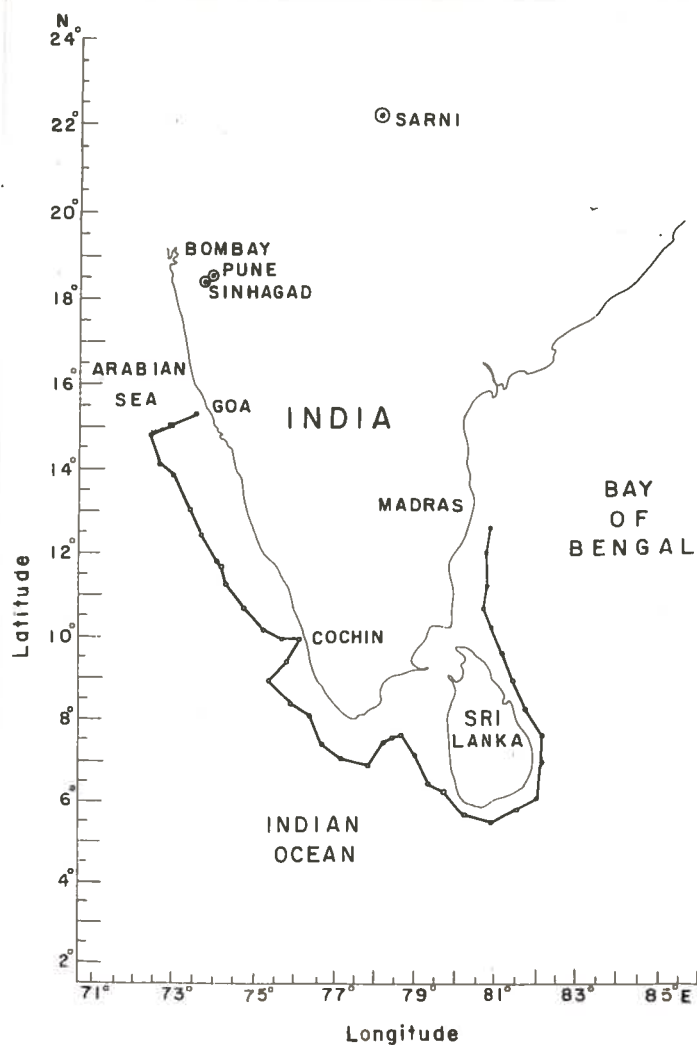


Figure 2.2 Map showing the cruise of research vessel 'Gaveshani' in the Arabian sea, Indian ocean and Bay of Bengal.

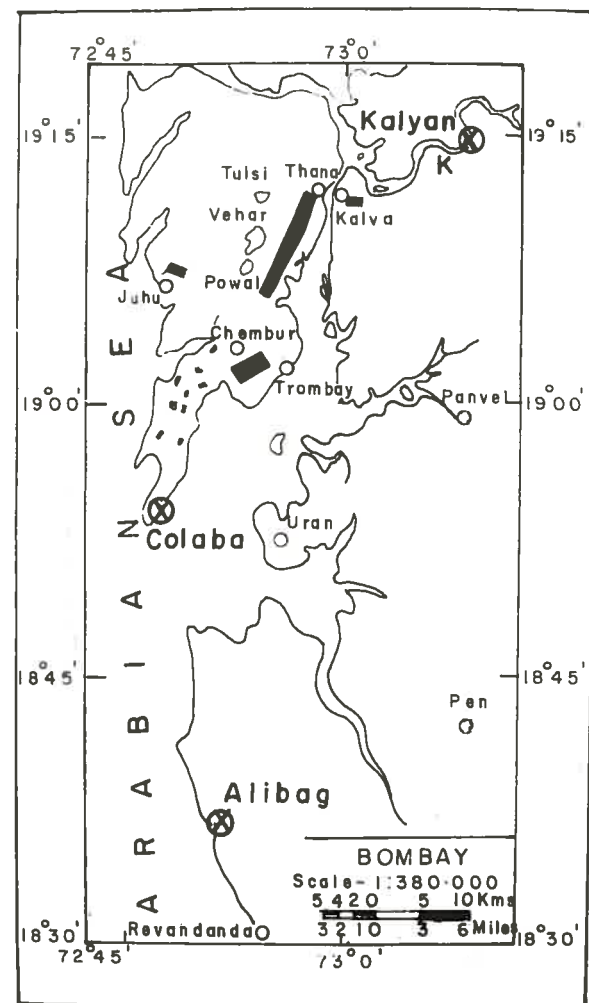


Figure 2.3 Locations of observational sites are shown by the symbol cross-in-circle in the map of Bombay region.

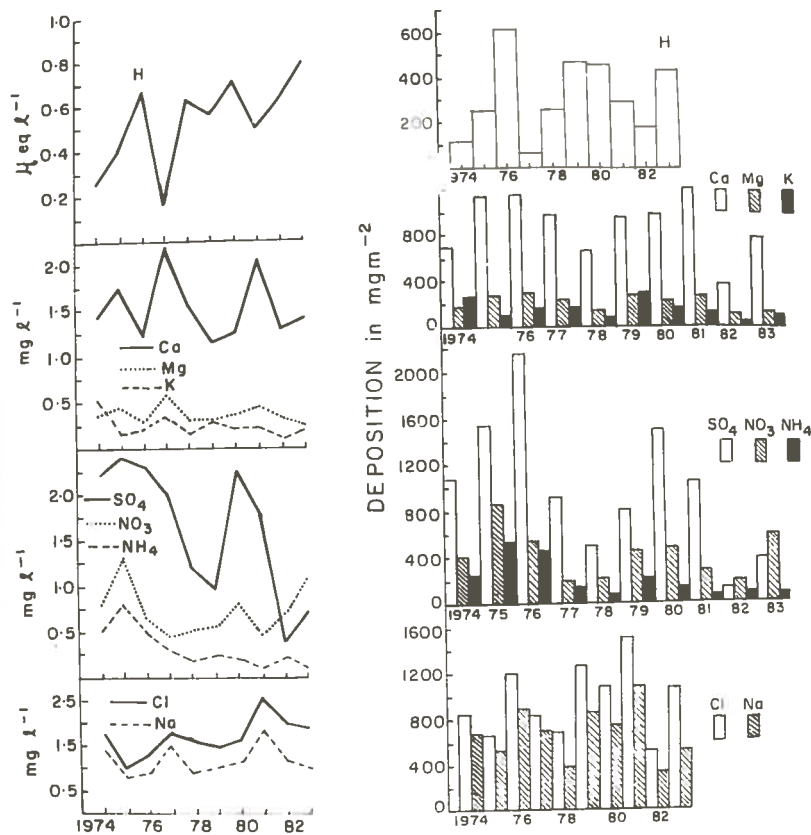


Figure 6.1 Average concentration of the major chemical components and their deposition in 10 monsoon seasons at Pune.

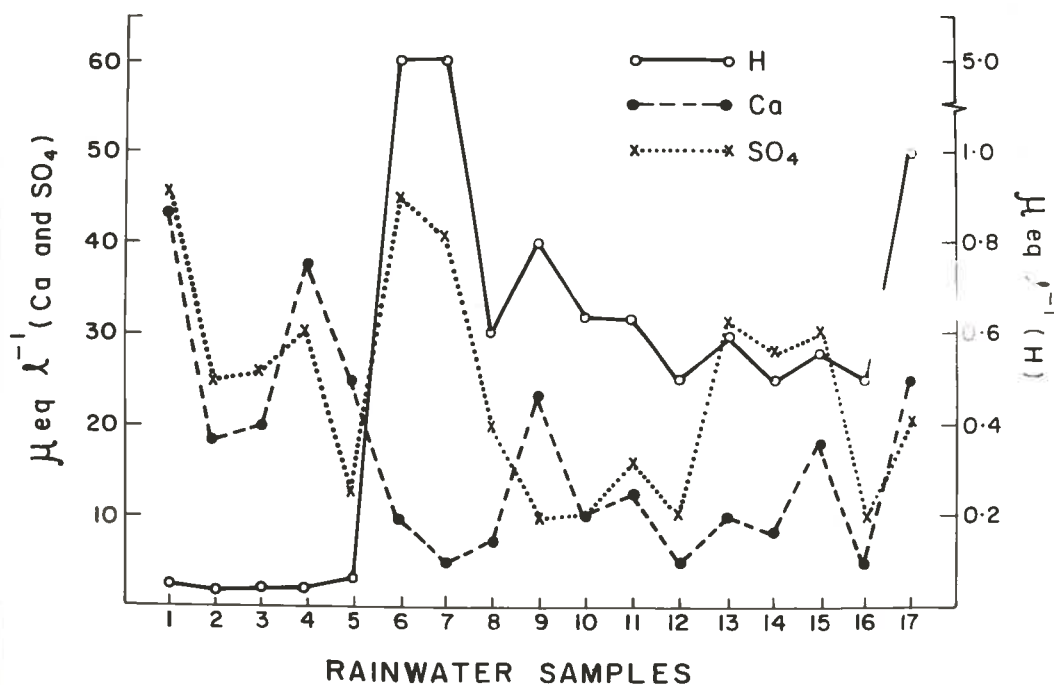


Figure 6.2 Variation of hydrogen, calcium and sulphate concentrations in rain water samples collected on 31 July 1965 at Delhi.

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Table 6.9 : Average concentrations in nano equivalent per cubic meter (neq m^{-3}) of anion and cation in TSP at seven locations in India.

TABLE 6.1 : Average concentrations in mg L^{-1} of major ionic components and pH values in rain water samples during 1974.

Location	Cl	SO ₄	NO ₃	NH ₄	Na	K	Ca	Mg	pH
Alibag	5.97	1.11	0.57	0.27	3.84	0.88	2.38	0.60	7.2
Colaba	4.14	2.58	0.40	0.51	3.12	1.13	2.56	0.64	7.1
Kalyan	3.95	5.20	1.92	0.38	2.36	1.02	1.86	0.47	5.7
Pune	1.72	2.20	0.80	0.50	1.39	0.53	1.43	0.36	6.6
*Chembur	5.00	20.20	—	2.10	2.20	1.10	3.10	0.68	4.8

*Sequeira, 1976

Table 6.2 : Average concentrations in mg L^{-1} of the major ionic components along with pH values at Sirur.

Year	Cl	SO ₄	NO ₃	NH ₄	Na	K	Ca	Mg	pH
1979	2.03	1.25	1.35	0.06	1.15	0.53	1.46	0.37	6.4
1980	2.29	1.19	2.37	0.05	1.02	0.43	2.27	0.53	6.5
1981	3.85	2.27	5.14	0.14	2.87	1.25	3.87	1.46	7.3
1982	2.39	0.90	1.69	0.04	2.31	1.14	6.51	0.79	7.4

TABLE 6.3 : Average concentrations in mg L^{-1} of major ionic components along with pH values at Delhi and Agra

Location	Year	Cl	SO ₄	NO ₃	NH ₄	Na	K	Ca	Mg	pH
Delhi	1965	2.52	1.23	-	0.23	1.83	0.42	4.83	-	7.0
	1984	2.54	2.73	2.54	0.53	1.75	1.28	2.95	0.62	6.1
Agra	1963	2.24	1.81	0.68	0.20	2.16	2.00	9.36	-	9.1
	1984	2.69	2.48	2.46	0.33	2.32	1.58	4.73	0.82	6.3

TABLE 6.4 : Ratio values of major ionic components to sodium at seven locations and the corresponding values for sea water.

Location	Cl/Na	Mg/Na	K/Na	Ca/Na	SO ₄ /Na
Alibag	1.55	0.16	0.23	0.62	0.29
Colaba	1.33	0.21	0.36	0.82	0.83
Kalyan	1.67	0.20	0.43	0.79	2.20
Pune	1.23	0.26	0.38	1.03	1.58
Sirur	1.31	0.34	0.45	1.91	0.82
Delhi	1.41	0.34	0.44	2.17	1.11
Agra	1.05	0.36	0.79	3.14	0.95
Sea water	1.80	0.13	0.036	0.038	0.25

TABLE 6.5 : Seasonal deposition of ionic components along with rainfall in the Bombay region.

Location	Deposition in mg m ⁻²								Rainfall (mm)
	Cl	SO ₄	NO ₃	NH ₄	Na	K	Ca	Mg	
Alibag	13504	2511	1289	611	8686	1991	5384	1357	2262
Colaba	9609	5988	928	1184	7242	2623	5942	1485	2321
Kalyan	7118	9370	3460	685	4253	1838	3352	847	1802

TABLE 6.6 : Correlation coefficients of pH with ionic components in rain water at Pune

	SO ₄	NO ₃	NH ₄	K	Ca	Mg
pH	-0.10	0.12	-0.01	0.27	0.56	0.43

TABLE 6.7 : Average concentrations of anions and cations in $\mu\text{eq L}^{-1}$ and pH values in rain water at different locations during 1974.

Location	Cl + SO ₄	NO ₃	\sum^{-}	NH ₄	Na + K	Ca + Mg	\sum^{+}	$\sum^{-} - \sum^{+}$	pH			
Colaba	117	54	6	177	28	136	29	128	53	374	-197	7.2
Alibag	168	23	9	200	15	167	23	119	49	373	-173	7.1
Pune	48	46	13	107	28	60	14	72	30	204	- 97	6.6
Kalyan	111	108	31	250	21	102	26	92	38	280	- 30	5.7
Chembur	141	421	-	562	117	96	28	155	56	452	+110	4.8

TABLE 6.8 : Concentrations of major ionic components and pH values in rain water collected at cloud base (CB) and at ground (G) at Pune.

Date	Level	Concentrations in $\mu\text{eq L}^{-1}$					Total	Mg	Total	H	pH
		SO ₄	NO ₃	Total	Ca						
14.7.1983	CB	11.5	7.0	18.5	25.5	14.2	39.7	0.79	6.1		
	G	21.8	30.3	52.1	94.5	25.0	119.5	0.05	7.3		
5.8.1983	CB	4.0	8.7	12.7	55.0	37.5	92.5	1.58	5.8		
	G	5.6	15.8	21.4	212.0	41.7	253.7	0.02	7.6		
28.8.1983	CB	6.7	5.9	12.6	47.0	10.0	57.0	1.00	6.0		
	G	18.5	21.0	39.5	156.0	36.7	192.7	0.10	7.0		
5.9.1983	CB	7.5	5.8	13.3	44.5	18.3	62.8	2.50	5.6		
	G	18.0	-	18.0	179.0	23.3	202.3	0.04	7.4		
Average	CB	7.4	6.9	14.3	43.0	20.0	63.0	1.45	5.8		
	G	16.0	22.4	38.4	160.4	31.7	192.1	0.05	7.3		

TABLE 6.9 : Average concentrations in nano equivalents per cubic meter
(neq m⁻³) of anion and cation in TSP at seven locations
in India.

Location	Cl + SO ₄	NO ₃	\sum^-			NH ₄	Na + K	Ca + Mg	\sum^+		
Sea region	205	21	38	264	23	163	8	37	38	269	- 5
Sinhagad	24	17	9	50	9	17	6	11	7	50	0
Raichur	14	19	17	50	48	17	11	44	24	144	- 94
Tuticorin	152	38	17	207	55	117	12	110	45	339	- 132
Pune	38	26	20	84	25	34	9	51	17	136	- 52
Delhi	56	48	54	159	18	37	14	129	20	218	- 59
Sarni	19	15	21	55	18	21	10	80	24	153	- 98