Role of aerosols in deciding pH of rainwater

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सार – वर्षा का स्वरूप क्षारीय है अथवा अम्लीय, यह जल में विलयषील प्रमुख अकार्बनिक गैसीय और उसी में घुलनषील मृदा से व्युत्पन्न कणों की सांद्रता पर आधारित होता है। यदि धनायन अम्ल की सांद्रता ऋणायन अम्ल की अपेक्षा अधिक होती है तो वर्षा क्षारीय और अम्लीय होती है।

पी. एच. एक प्रमुख प्राचल है जो वर्षा के स्वभाव को दर्षाती है। पी. एच. के पैमाने पर बेट 0 से 14 पर यदि विलयषील का पी. एच. 5.65 से कम होता है तो यह अम्लीय है और 5.65 से अधिक होता है तो क्षारीय है।

इस षोध–पत्र में क्षारीय श्रेणी और अम्लीय श्रेणी में पी. एच. वाले वर्षा के जल में रसायनिक संयोजन में पाई गई भिन्नता का अध्ययन किया गया है। इस उद्देष्य के लिए 1988–97 के दौरान इलाहाबाद, जोधपुर, मोहनबाड़ी और नागपुर में हुई वर्षा के रसायनिक आंकड़ों पर विचार किया गया है। इस आधार पर ए. पी. डब्ल्यू एम. और एस. डी. तैयार किए गए। अम्लीय श्रेणी और क्षारीय श्रेणी में ए. पी. डब्ल्यू एम. के मानों पर विचार करते हुए वर्षा के रसायनिक आंकड़ों को अलग किया गया और उनकी तुलना की गई। इसमें संभाव्य धनायन अम्ल–ऋणायन अम्ल के संयोजकों में सहसंबंध के गुणांक परिकलित किए गए हैं।

यह देखा गया है कि 1997 के दौरान न्यूनतम पी. एच. मान (मासिक मान) अभिलेखित किए गए – मोहनबाड़ी में (3.77), नागपुर में (4.12) दोनों अम्लीय श्रेणी में हैं। इस षोध–पत्र में किए गए अध्ययन की अवधि में अम्लीय श्रेणी में पी. एच. मानों की घटनाओं की आवृति मोहनबाड़ी में सबसे अधिक (66%) थी। जोधपुर में रिकार्ड की गई सभी पी. एच. मानों में पाई गई क्षारीय श्रेणी से यह पता चलता है कि जोधपुर में मृदा से व्युत्पन्न क्षारीय कणों का प्रभाव रहता है। धनायन अम्लों में Ca^{+2} से सभी धनायन अम्लों में इसके प्रभाव का पता चलता है। वर्ष 1997 में जोधपुर में Ca^{+2} (9.27 मि. ग्रा. ⁄ ली.) के उच्चतम ए. पी. डब्ल्यू एम. मान अभिलेखित किए गए।

इन आंकड़ों की भी विष्ष मौसम संगठन प्रयोगषाला से अनुकरित अम्लीय वर्षा के नमूनों से विष्लेषित आंकड़ों और अन्य गैर–विभागीय आंकड़ों के साथ तुलना की गई है।

इस षोध–पत्र में इनसे प्राप्त हुए परिणामों पर विचार–विमर्ष किया गया है।

ABSTRACT. Nature of precipitation – alkaline or acidic – depends upon the concentration of major water soluble inorganic gaseous and soil derived particulates dissolved in it. If concentration of cations is higher than that of anions, the precipitation becomes alkaline and *vise-a-versa*.

pH is the main parameter indicating the nature of precipitation. If pH of the solution is < 5.65, it is acidic and > 5.65, alkaline, in the pH scale ranging between 0 & 14.

Difference in the chemical composition of rainwater having pH in the alkaline range and acidic range has been studied in this paper. For this purpose, precipitation chemistry data of Allahabad, Jodhpur, Mohanbari and Nagpur for the period 1988-97 have been considered. APWM & S.D. have been worked out. Precipitation chemistry data considering APWM values in acidic range and in alkaline range have been separated and compared. Coefficients of correlation have been calculated in possible cation-anion combinations.

It is seen that the lowest pH values (monthly mean) have been recorded during 1997 – MHB (3.77), NGP (4.12), both in acidic range. % Frequency of occurrences of pH values in acidic range was the highest at Mohanbari (66%) in the study period. Jodhpur recorded all pH values in alkaline range indicating influence of soil derived alkaline particulates. Among cations Ca^{+2} has shown its dominance over all cations. Jodhpur has recorded the highest APWM value of Ca^{+2} (9.27mg/lit) in 1997.

Data have also been compared with WMO Laboratory simulated acid rain sample analysis data and other non-departmental data.

Results are discussed in the paper.

Key words – pH, Chemical composition, APWM, Rain water.

1.   Introduction

The importance of chemical analysis of rain water has been realized during last few decades, since pollution has increased due to increasing population and industries. Changed land used pattern and excessive fossil fuel burning due to tremendous increase in the vehicles have pumped enormous amounts of aerosols in the atmosphere responsible for pollution.

In India, prior to the establishment of BAPMoN (Background Air Pollution Monitoring Network) in 1973-75, Mukherjee, (1964) studied the acidity of monsoon rain water and H^+ ion concentration at Calcutta. He reported pH value very close to 7.0. Since the establishment of network of 10 stations (Fig. 1), under BAPMoN – WMO Project (now GAW), chemical analysis of monthly mixed rainfall samples is being carried out regularly at Air pollution Laboratory, O/o ADGM (R), Pune, to determine concentrations (mg/lit) of major cations and anions, along with pH and conductivity measurements. Many workers have studied the data to find out the influence of various sources on chemical composition of rainwater. Maske and Krishna Nand (1982) studied precipitation chemistry data of BAPMoN stations for 1979 and concluded that the Bay of Bengal and the Arabian Sea are the major sources of chloride and sodium in rainwater. Krishna Nand pointed out that due to high quantity of natural suspended particulate matter, which is mainly alkaline in nature, the pH of rainwater remains in the alkaline range in India. Mukherjee, *et al.* (1986) found out that pH of rainwater over Indian Oceanic areas is also in basic range. Varma (1989) studied impacts of soil derived aerosols on precipitation acidity and attempted to regionalise Indian continent on the basis of pH results obtained. According to this, part of NE India and East coast are highly sensitive to acid rains, (pH< 6.0).

In recent studies carried around an industrial region in Mumbai, Naik, *et al.* (2002) reported the influence of soil derived aerosols on alkaline pH values of rainwater and influence of emissions of sulphur and nitrogen from fossil fuel burning, vehicular traffic and other industries on acid rain at Kalyan.

In the present studies, an attempt has been made to find out difference in chemical composition of major inorganic water soluble constituents in precipitation
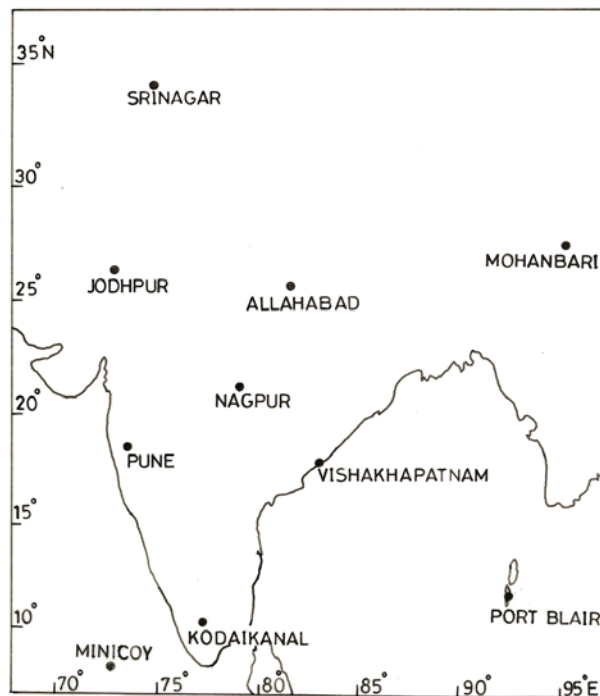

Fig. 1.   Background air pollution monitoring network (BAPMoN) Stations in India

having pH in acidic$\leq$ (5.56) and non -acidic (alkaline) (> 5.65) range.

2.   Methodology

Specially designed wooden precipitation collector with stainless steel cover and polyethylene funnel and two litre capacity polyethylene bottle is used for rainwater collection. The precipitation collectors are covered during non-rainy period. These are opened and washed with distilled water just before rain is expected to avoid dry deposition. Daily collected rainfall sample is filtered through whatman - 41 filter paper.

pH and conductivity of this sample is measured immediately and this sample is transferred to a bigger container. 500 ml of such monthly mixed rainfall sample is received at Pune, Central Air Pollution Laboratory in polyethylene bottle for further analysis. These samples

TABLE 1

Details of the stations

S. No.	Name	Soil texture	Lat (°N)	Long (°E)	Altitude (m)
1.	Allahabad	Continental Alluvial	25° 27'	81° 44'	98
2.	Jodhpur	Continental Arid	26° 18'	73° 01'	217
3.	Mohanbari	Humid Alluvial	27° 29'	95° 01'	111
4.	Nagpur	Continental	21° 06'	79° 03'	310

TABLE 2

Annual precipitation weighted mean pH data 1988-97

Year	Allahabad	Jodhpur	Mohanbari	Nagpur
No. of rainfall samples studied	62	47	106	82
1988	5.51	6.68	4.91	5.42
1989	6.68	7.79	4.65	4.88
1990	5.95	7.72	5.19	4.93
1991	7.32	-	4.58	6.81
1992	-	-	4.73	6.74
1993	-	7.79	5.96	4.67
1994	-	6.56	4.88	5.76
1995	6.29	7.98	4.96	5.30
1996	5.51	7.35	4.83	5.83
1997	5.74	7.57	4.57	4.61

are stored in refrigerator till the chemical analysis is over, to avoid contamination.

Pye-unichem double beam atomic absorption spectrophotometer with air acetylene flame was used to determine concentration (mg/lit) of cations – Ca^{+2}, Na^+, Mg^{+2}, and K^+. The concentration of NH_4^+, NO_3^-, Cl & SO_4^{-2} were determined by calorimetric method. Double beam UV-visible spectrophotometer (Shimadzu, Japan) was used to measure absorbance at specific characteristic wave length of each anion radical. pH was measured with digital pH meter with combined glass electrode. Wind roses of these stations were used to emphasize the influence of wind direction and speed on the chemical composition of rain water.

Location of sampling sites namely Allahabad, Jodhpur, Mohanbari and Nagpur are shown in Fig. 1 and details are given in Table 1. These four stations form a part of BAPMoN, now called as GAW (Global Atmosphere Watch) network. These are regional category stations with minimum parameter measurement programme.

3. Result and discussions

(*i*) *pH Measurement*

Acidity in a solution is synonymous with the presence of hydrogen ions in the solution. A common measure of acidity is pH. It is the first indicator of the nature of precipitation. pH ranges from 0 to 14 with 7 indicating neutral solution, in extremely unpolluted, ideal atmospheric conditions. However, due to the dissolution of carbon dioxide (CO_2) present in the atmosphere, (and formation of carbonic acid), pH of even uncontaminated rain water reduces to 5.65 at 20° C. (WMO No. 299). Deviation from this value indicates that ions other than HCO_3^- and H^+ are present in the sample. Hence pH< 5.65 is considered in the acidic range.

pH of precipitation depends on various water soluble constituents. These constituents are of two types – soil derived and gaseous. These can be marine and anthropogenic also. Variety of sources of these air borne particulates is available in nature – dust picked up by winds, smoke from naturally set fires, pollens from

TABLE 3

Mean APWM concentration (mg/lit), standard deviation and µeq/lit of major water soluble constituents

Element	Allahabad		Jodhpur		Mohanbari		Nagpur (Ac)		Nagpur (Alk)	
	APWM/SD	ueq/lit	APWM/SD	ueq/lit	APWM/SD	ueq/lit	APWM/SD	ueq/lit	APWM/SD	ueq/lit
Cl	1.91/1.09	55.43	4.39/2.12	123.40	0.89/0.66	25.83	0.83/0.12	24.10	1.11/0.60	32.21
SO_4	2.40/1.60	49.97	4.46/3.56	92.86	1.44/0.95	29.98	1.92/1.32	39.97	1.52/1.98	31.65
NO_3	11.81/5.09	184.47	4.97/3.56	77.63	6.16/2.71	96.22	7.54/5.79	117.77	5.56/2.27	86.85
Ca	3.18/1.47	158.68	6.27/2.53	312.87	0.92/0.64	45.91	1.58/0.78	78.84	1.76/0.67	87.82
Na	3.14/1.57	136.59	4.27/2.53	185.75	0.55/0.67	23.93	0.62/0.15	26.97	0.41/0.11	17.83
K	1.84/1.79	47.05	1.71/0.97	43.72	0.73/0.72	18.67	0.51/0.17	13.04	0.59/0.37	15.09
Mg	1.22/0.98	101.63	0.88/0.67	73.30	0.16/0.21	13.33	0.32/0.22	26.66	0.32/0.18	26.66
NH_4	0.25/0.21	13.86	0.06/0.05	3.33	0.64/0.32	35.47	0.40/0.25	22.17	0.25/0.36	13.86
pH	6.14/0.67	-	7.43/0.53	-	4.92/0.42	-	4.97/0.31	-	6.29/0.57	-
H Moles/lit	0.72 E - 06	0.72	0.37 E - 06	0.036	12.20 E - 06	11.90	10.71 E - 06	10.61	0.51 E - 06	0.51

forests, gases, particulates from volcanoes, sea-spray, combustion of fossil fuel, soil erosion etc. Momin *et al.* (1999).

According to above concept, chemical analysis data with APWM pH value in acidic range (<5.65) and in alkaline range (> 5.65) have been separated and difference between chemical composition of major inorganic constituents (mg/lit) has been studied to find out the role of aerosols in deciding the nature of rain – acidic or alkaline. These data have been compared with WMO laboratory simulated acid rain sample analysis data and other two non departmental stations data – namely Kalyan and Chembur.

APWM pH values for four stations for the period 1988-97 are given in Table 2. It is seen that at Jodhpur all pH values are in alkaline pH range (>5.65), while at Mohanbari all pH values are in acidic range (< 5.65). Nagpur exhibits mixed character with four APWM pH values in alkaline pH range (1991, 1992, 1994 & 1996) and at Allahabad, only two APWM pH values are marginally in acidic range (1988, 1996). This supports the earlier studies of Mukhopadhyay, *et al.* (1992) which state that there is a major downward gradient in pH of rainwater as one travels from west to east; Jodhpur recording the highest pH values while Mohanbari, the lowest.

The highest pH value (monthly mean) recorded is 9.38 at Jodhpur in April 1997, while the lowest value is 3.77 at Mohanbari in October 1997.

It is seen that all rainfall samples collected at Jodhpur were alkaline in nature, as expected, as the soil in this region is sandy, loose, and sand storm, dust raising winds create abundant soil derived aerosols, which are alkaline in nature. Allahabad recorded 16% (10 samples), Nagpur 40% (33 samples) and Mohanbari recorded 66% (71 samples) in acidic range of pH.

(*ii*)   *Chemical composition*

Mean APWM concentration (mg/lit) values of water soluble constituents along with S.D. and µeq/lit for all four stations are given in Table 3. Nagpur data with acidic APWM pH and alkaline APWM pH have been separated out as shown in the table.

Soil derived aerosols mainly contain particulates of Ca, Mg, K etc. which are mostly alkaline in nature. Seasonal trend of high concentration of constituents in April, May reducing upto September may be attributed to strong SWly monsoon current bringing more and more sea spray and land oriented aerosols. Strong NElies prevail over Mohanbari, throughout the year. These are mainly land oriented, but fail to produce sufficient quantities of soil derived aerosols due to climatic and orographic features of the region. Hence less seasonal variations are noticed. On the other hand gaseous particles of SO_2 and NO_x ($NO + NO_2$) are acidic by nature. These are the main contributors to precipitation acidity. They dissolve in rainwater to give acidic nature to the rainfall by forming dilute H_2SO_4 and HNO_3. Hence rainfall analysis

Cation Composition at different stations
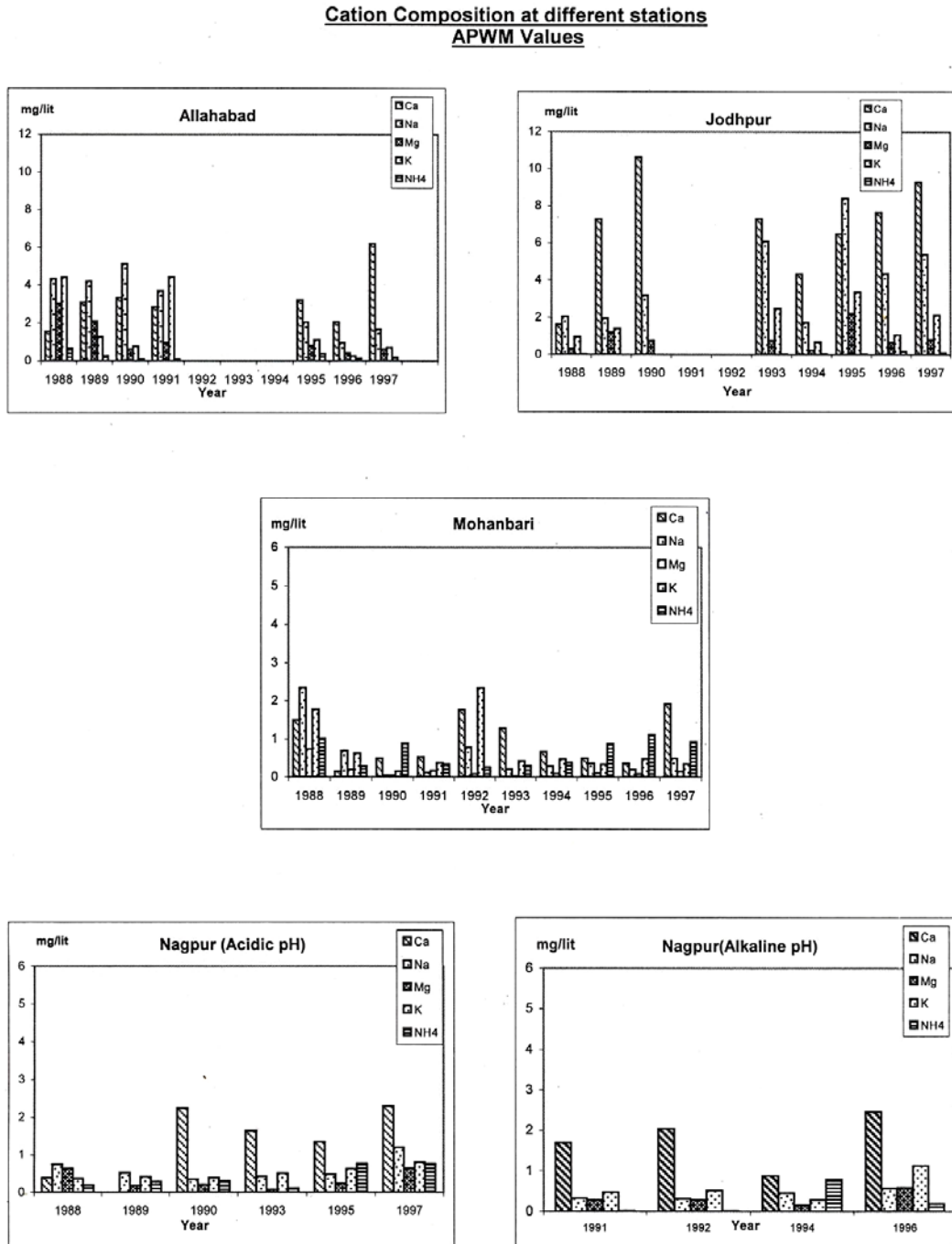**APWM Values**

Fig. 2. Cation composition at different stations APWM values

is very useful tool to find out difference in major inorganic water soluble constituents in acidic and non-acidic (alkaline) rainfall as most of the water soluble particulate matter (about 80%) is removed by the rain. Khemani *et al.* (1987) have reported that the rainwater drop just emerging out of the cloud has pH substantially lower than that of CO_2 equilibrated value of 5.6, *i.e.*, in the acidic range. The water soluble soil derived and gaseous aerosols present in the atmosphere through which raindrop travel thousands of metres are responsible for the nature of rainfall – alkaline or acidic at each location. However, it is very much influenced by the rainfall amounts, diluting concentration of most of the ions with higher rainfall amounts.
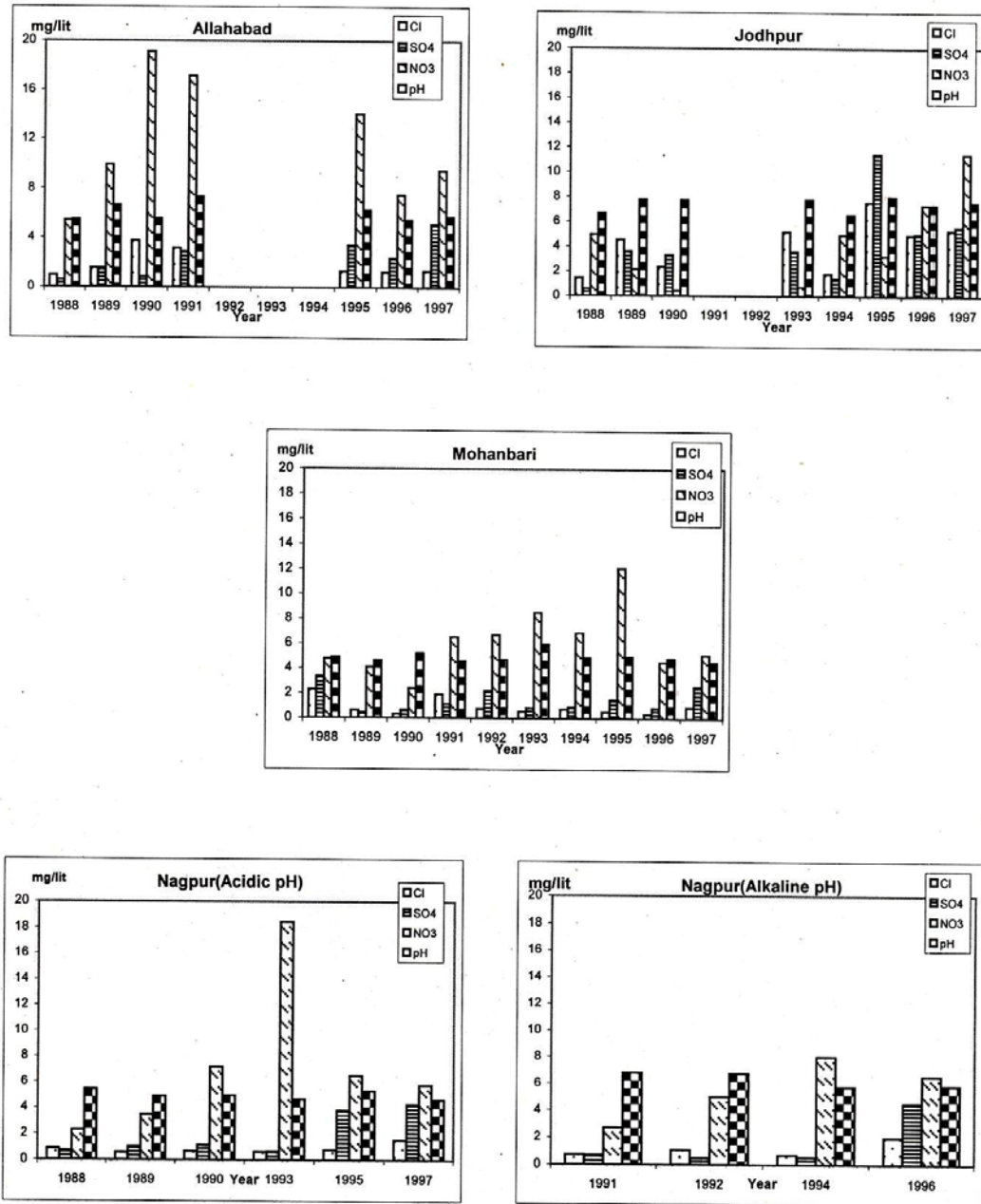
**Fig. 3.** Anion composition at different stations APWM values

It is seen from Table 3 that all APWM concentration values are the lowest at Mohanbari except NO_3 (6.16mg/lit) value which is higher than the NO_3 concentration value at Jodhpur (4.97 mg/lit). the higher concentration of NO_3 at Mohanbari may be due to excessive thunderstorm activity occurring at Mohanbari.

It has been reported by Krishna Nand *et al.* (1983) earlier that nitrate concentrations in rainfall are positively correlated with thunderstorm activity. Daily evening and late night line thunderstorm activity during pre-monsoon and post monsoon months occurring at Mohanbari may be responsible for conversion of atmospheric nitrogen into

TABLE 4

Average ionic concentration (mg/lit) of major inorganic components of precipitation 1988-1997

Element	Alkaline pH			Acidic pH				
	Nagpur	Allahabad	Jodhpur	Mohanbari	Nagpur	Kalyan	Chembur	WMO
Cl	1.11	2.67	4.37	0.96	1.21	4.75	5.00	1.496
SO$_4$	1.65	4.09	4.53	2.35	2.42	5.30	20.20	0.659
NO$_3$	8.50	14.68	9.48	7.11	9.62	4.10	NR	0.35
Ca	3.09	4.81	8.92	1.39	2.69	2.60	3.10	0.201
Na	0.77	3.44	4.14	1.12	0.81	3.40	2.20	0.901
K	0.97	2.33	2.73	0.93	1.00	0.39	1.10	0.139
Mg	0.58	1.48	1.34	0.51	0.54	0.58	0.68	0.094
NH$_4$	0.35	0.55	0.17	0.91	0.52	0.26	2.10	0.325
H	0.33	0.25	0.02	4.17	4.26	5.25	15.84	92.68
pH	6.48	6.60	7.60	5.38	5.37	5.28	4.80	1.033
% Anions	66.15	62.97	51.50	68.19	70.70	66.19	73.29	60.14
% Cations	33.84	37.02	48.48	31.81	29.56	33.81	26.72	39.85
% NaCl	11.04	17.94	23.85	13.61	10.74	38.12	20.94	57.55

NO, NO$_2$ radicals and ultimately to HNO$_3$ particles by following reactions :

$$N_2 + O_2 \rightarrow 2\,NO$$

$$2NO + O_2 \rightarrow 2NO_2$$

$$4NO_2 + O_2 + 2H_2O \rightarrow 4HNO_3$$
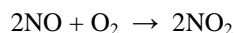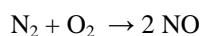
Mohanbari gets rain throughout the year. Damp, cold, cloudy weather prevails at the station for most of the year. Humid climate cuts down on soil derived aerosols. Study of wind roses indicates that NEly wind is predominant at the station throughout the year. This is unable to transport aerosol rich air to the station due to hilly terrain and thick vegetation cover, forest. Cumulative effect of all these factors is the lowest concentration (mg/lit) of all constituents in the rainwater. Among anions, Mohanbari has recorded the lowest APWM concentration (1.44mg/lit) of SO$_4^{-2}$ while Jodhpur has recorded the highest concentration (4.46mg/lit). It is seen that NO$_3^-$ concentration is higher at all the stations with the highest concentration (11.81mg/lit) at Allahabad Fig. 3. Similar results have been obtained by the Shende and Gaikwad (2001) earlier also. It is seen from the data of 1988-97, that SO$_4^{-2}$ is showing decreasing trend while NO$_3$ is showing increasing trend at Mohanbari. At Kalyan, also Naik *et al.* (2002) have observed similar trends in the 20 year period.

Among cations Ca^{+2} and Mg^{+2} are the main soil derived buffering elements, neutralizing acidic aerosols. These show the lowest concentration (0.92 mg/lit &

0.16mg/lit) at Mohanbari as compared to other stations, though 0.92mg/lit is the highest concentration at the station. Hence there is less neutralizing effect on the acidic aerosols at Mohanbari. The concentration of K$^+$ (APWM value) – 0.73mg/lit is the next higher concentration and higher than recorded at Nagpur – 0.51 mg/lit – acidic pH precipitation data and 0.59 mg/lit – alkaline pH precipitation data. Thick vegetation cover in NE region gives huge amounts of wood for domestic and other purposes, wood-cutting saw mills and small scale industries pertaining to wood-furniture, toys, household articles etc. are the main source of earning in this region. K is the essential element of plant, wood, which is emitted during combustion and other processing of wood. In all four major cations are Ca^{+2}, Na$^+$, K$^+$ & Mg^{+2}, Ca^{+2} showed the highest concentration (0.93 mg/lit), K$^+$ is next to it (0.73 mg/lit) at Mohanbari.

But Na$^+$ has recorded lower concentration of 0.55 mg/lit. Mohanbari is located in the far NE end corner of Indian continent, in hilly terrain. Sea spray aerosols are the main source for Na$^+$ & Cl$^-$ radicals over Indian region. Sea spray aerosols, mainly of SW monsoon current have to travel a very long distance before these reach NE region. Hence number of sea–spray aerosols reaching the station is considerably reduced due to land friction. Same results are seen at Nagpur, which is located on the central peninsula of Indian continent. Na$^+$ concentration have recorded low value – 0.62mg/lit, as compared to that of Ca^{+2} – 1.58mg/lit in acidic pH data, while for alkaline pH data, Na$^+$ concentration –0.41mg/lit which is lower than that of acidic pH data, but Ca^{+2} concentration 1.76mg/lit is higher. The concentration of Na$^+$ is very close to that
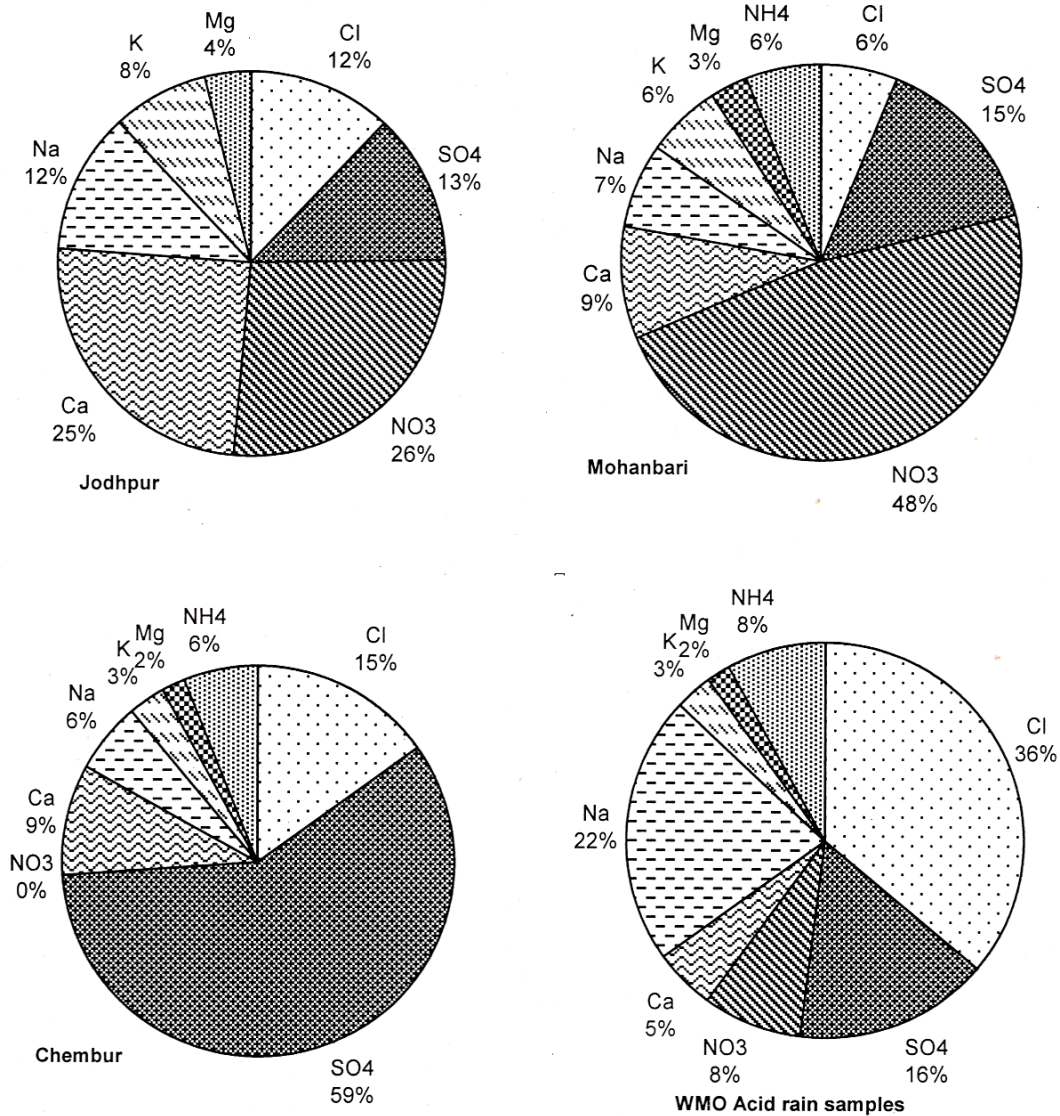
Percentage composition of major ions in rainwater samples

Fig. 4. Percentage composition of major ions in rainwater samples

of Ca^{+2} at Allahabad *i.e.*, Na^+ = 3.14 mg/lit and Ca^{+2} = 3.18mg/lit. Similarly concentration of Na^+ is higher at Jodhpur 4.27 mg/lit than its concentration at other GAW stations. This indicates that sodium is also derived from the salt particles available (NaCl) in that region.

It is observed that (Table 3), concentration of all cations is higher at Jodhpur and Allahabad as compared to other stations. Fig. 2. This may be due to loose soil at Jodhpur – desert sand and river banks (sand) where Allahabad is located. Therefore the precipitation at these stations is mostly alkaline in nature with high pH, Jodhpur (7.43) and Allahabad (6.14). Earlier studies of Khemani (1993) reported that as soil in India is rich with alkaline components like Ca, K, and Mg alkaline aerosols released from it have large influence on the pH of rainwater in India.

TABLE 5

Ratios of various chemical components with Na (by weight)

	SO_4/Na	Cl/Na	Ca/Na	Mg/Na	K/Na
Sea water	0.25	1.80	0.038	0.119	0.036
Allahabad	1.19	0.78	1.40	0.43	0.68
Jopdhpur	1.09	1.05	2.15	0.32	0.66
Mohanbari	2.10	0.86	1.24	0.45	0.83
Nagpur (Acidic pH)	3.00	1.49	3.32	0.67	1.23
Nagpur (Alkaline pH)	2.14	1.44	4.01	0.75	1.26
WMO Samples	0.73	1.66	0.22	0.10	0.15
Kalyan	1.56	1.40	0.76	0.17	0.11
Chembur	9.18	2.27	1.41	0.31	0.50

At Nagpur, in case of alkaline pH precipitation, concentration of SO_4^{-2} and NO_3^- is less, 1.52mg/lit and 5.56mg/lit, as compared to that of acidic pH precipitation data, 1.92mg/lit and 7.54mg/lit respectively. Also, concentrations of Ca^{+2} and K^+ are higher in alkaline pH precipitation – 1.76mg/lit and 0.59mg/lit, than that of acidic pH precipitation data – 1.58mg/lit and 0.51mg/lit respectively. The relative contributions of primary soil derived aerosols (Ca, K & Mg) and secondary aerosols (SO_4 & NO_3) in rain water decide the acidity in rainwater. Hence higher concentrations of these radicals make precipitation alkaline in nature.

3.   Comparison of data

Average ionic concentration (mg/lit) of major water soluble inorganic constituents of precipitation having pH in alkaline range *i.e.*, > 5.65 and acidic range *i.e.*, < 5.65 are given in Table 4. Data of two non-departmental stations namely Kalyan and Chembur have been taken for comparison. WMO acid rain sample analysis data of April and October 2002 have also been considered for comparison. WMO acid rain samples are laboratory simulated samples. These are sent to many GAW member countries for inter comparison of data twice in a year, April and October. About 42 countries participate in this inter comparison. The results obtained are sent to WMO-GAW Precipitation Chemistry Data Centre at Albany University, New York, USA. for inter-comparison and assessment of the quality of data.

Fig. 4 shows relative percentage (%) contribution of major cations and anions for GAW stations namely Jodhpur with alkaline pH precipitation, Mohanbari – acidic pH precipitation, a non departmental station Chembur – with the lowest pH of precipitation and WMO acid rain analysis results. It is seen that in acidic pH

rainwater samples, % contribution of anions is more than 65%. Jodhpur, with the highest APWM pH of 7.60, exhibits nearly equal % contribution of cations and anions – 48.5% and 51.5% respectively. It is seen from Table 4 that, at all GAW stations, under study, average ionic concentration / contribution of NO_3^- is higher than that of SO_4^{-2}, Jodhpur – 9.48mg/lit and 4.53mg/lit, Mohanbari – 7.11mg/lit and 2.35 mg/lit. But at Kalyan and Chembur, which are under the influence of industries, SO_4^{-2} concentration is higher than NO_3^- concentration Kalyan – 5.30mg/lit and 4.10mg/lit, Chembur – 20.2mg/lit (SO_4^{-2}). NO_3 data are not available. It is noticed that H^+ ion concentration (moles/lit) is the highest at Chembur 15.84. This indicates the highest acidic nature of rainwater sample among all stations under study.

It is noticed that % sea salt (NaCl) contribution is maximum at Kalyan – 38%, which is in the vicinity of the Arabian Sea. Next higher % contribution is 24% at Jodhpur. Higher contribution of NaCl at Jodhpur clearly indicates availability of other source sodium chloride at the station or some NaCl molecules may be available in the nearby areas which dissolve in the precipitation. The lower % contribution of Cl^-, 18% at Allahabad, 11% at Nagpur and 14% at Mohanbari support the hypothesis of loss of Cl^- ions, due to friction, as sea-spray aerosols travel deep into land.

The % contribution of SO_4^{-2} is maximum (59 %) at Chembur. This indicates very high pollution of sulphur in the region. Kalyan is next to it with 25% contribution, while all other GAW stations remain below 15% contribution. % contribution of NO_3^- is higher at GAW stations, above 40%, except at Jodhpur, where it is 27%. This is also indicative of less pollution at Jodhpur.

The comparison of WMO laboratory simulated acid rain samples' chemical analysis data with other natural

TABLE 6

Coefficient of correlation (r) among ionic species

Species	Jodhpur	Allahabad	Mohanbari	Nagpur Alkaline pH	Nagpur Acidic pH
Cl/Na	0.65	0.71	0.73	0.49	0.52
K/Cl	0.61	0.54	0.43	0.64	0.52
SO_4/Ca	0.75	0.60	0.39	-0.12	0.33
Ca/Cl	0.49	0.50	0.53	0.62	0.39
Na/Cl	0.26	0.36	0.43	0.69	0.15
Mg/Cl	0.84	0.43	0.56	0.77	0.47
Ca/Mg	0.73	0.35	0.31	0.63	0.17
K/Ca	0.46	0.06	0.36	0.89	0.34
K/SO_4	0.52	0.08	0.38	-0.04	0.21
Ca/NO_3	0.31	-0.12	0.31	-0.13	0.42

precipitation sample analysis data is not appropriate, since laboratory simulated samples can have desired concentration of various components/constituents. But just to have an idea about how chemical composition of acid rain samples having pH purely in acidic range very, comparison is made. It is seen that % contribution of anions is 60.14% while that of NaCl is 57.55% (Table 4). Such a high % contribution of NaCl is not observed in the nature. Also in low pH precipitation analysis data % contribution of anions is nearly 70% or more, but in WMO acid rain samples, it is only 60.14%, the lowest in all data sets, still the pH is very low. This is because concentration of Ca^{+2} is low 0.201mg/lit as compared to other natural rainfall samples. In nature, the soil mainly contains calcareous compounds like sulphates, dolamites, carbonates and bicarbonates in abundance. Calcium is the main constituent of soil crust. Hence Ca^{+2} concentration is always higher in rainfall samples. Such a low concentration of Ca^{+2} is not experienced in Indian rainfall samples. Ca^{+2} is the main buffering element of acidic radicals in the rain. It is seen from Table 4 that concentration of all cations – Ca^{+2}, K^+ and Mg^{+2} is kept much low. Even at Mohanbari concentration of these cations is much higher. Chembur also shows higher concentration of these radicals. The concentration of NH_4 has been kept the lowest. Ammonia produced in the anthropogenic reaction has a very large solubility. A small quantity of ammonia is able to affect pH of sample considerably. The low concentration of these elements is unable to neutralize acidic components and therefore pH remains low (4.033).

4.   Ionic correlation

Coefficient of correlations (CC) has been worked out in various possible combinations of anions and cations. These are given in Table 6. Cl/Na shows higher

correlation at Allahabad and Mohanbari is 0.71 and 0.73 respectively, though % contribution is lower at these stations. This indicates influence of marine air. Na and Cl ions mainly originate from a common source of sea salt. At Jodhpur CC between SO_4/Ca – 0.75, Mg/Cl – 0.84, K/Na – 0.80 is higher than Na/Cl – 0.65. This shows loss of some Cl ions as sea spray aerosols travel a longer distance into land, Eriksson, (1960). Higher CC also indicates that sulphates and chlorides of Ca and Mg are the predominant soil derived aerosols at Jodhpur. Species Ca and Mg are essential components of soil. This is supported by high CC between them (0.73). This also suggests the common origin of these aerosols. All these features indicate that wind carried dust and soil play significant role in chemical composition of rainwater. At Allahabad, Mg/SO_4 (0.40), SO_4/Ca (0.60), show higher correlation, next to Na/Cl (0.71). Sulphates of Ca and Mg are also main soil components. Earlier Mukhopadhyay *et al*. (1992) has also reported this. At Nagpur, chemical composition data with acidic pH (APWM) and alkaline pH (APWM) have been separated out and studied. It is seen that CC between Ca/Cl (0.62), Mg/Cl (0.77), K/Ca (0.89), K/Cl (0.64) is higher in alkaline pH rainfall samples, *i.e*., soil derived aerosols dominate when precipitation is alkaline in nature. But in acidic pH rainfall samples, all these CC values are very low, while SO_4/Ca (0.33), NO_3/Ca (0.42), NO_3/Na (0.27), SO_4/K (0.21) are higher as compared to alkaline pH data of Nagpur. This indicates that SO_4 and NO_3 are not soil derived aerosols at Nagpur. This suggests the gaseous reactions occurring in the atmosphere.

In combination CC, Jodhpur has recorded the highest value of sulphate with cations (0.97), while nitrate has shown the lowest or even –ve correlation with cations. (NGP Alkaline data). All stations under study show somewhat same results, *i.e*., higher CC with SO_4^{-2} and low CC with NO_3^- Carbonates and sulphates of Ca^{+2}, Mg^{+2}, K^+ are commonly available in soils of Indian continent. But NO_x (NO + NO_2) is mainly derived from gaseous emissions of automobiles of all types *viz*., trucks, cars, buses etc., DG sets, household daily used heaters, stoves etc. which finely converts into NO_3^- radical Kumar (1998).

At Mohanbari, APWM pH values during the decade 1988-97 are in acidic range, only one value of 1993 is marginally in alkaline range (5.96). CC values of K/Cl, SO_4/Ca, Mg/SO_4 (Table 6) are also low as compared to Allahabad and Jodhpur. These two stations have recorded pH values of precipitation in alkaline range. Between acidic pH data and alkaline pH data of Nagpur, alkaline pH data shows –ve CC between NO_3/Ca, NO_3/Na, K/NO_3, SO_4/Ca, K/SO_4, while acidic pH data shows +ve CC. This indicates that SO_4^{-2} and NO_3^- are main precursors in acidic precipitation. Thermal power

plants located in Nagpur region may have enhanced effect on these concentrations.

5.   Ratios of various species

It is a practice to calculate the ratios of various species of rainwater by weight with sodium (Na^+) and to compare these to the similar ratios of sea water. This helps in finding out the marine influence on the precipitation composition. Such ratios have been given in Table 5. It is seen that at GAW stations under study, SO_4/Na and Cl/Na ratios show rise as compared to earlier ratios of 1976-87.

SO_4/Na : ALB – 0.57 → 0.76,   JDP – 0.456 → 1.04,
MHB – 1.608 → 2.62,   NGP – 1.203 → 3.71

Cl/Na : ALB – 0.542 → 0.61, MHB – 1.477→ 1.62,
NGP – 0.847 → 2.70

Rise in SO_4/Na indicates rise in SO_4^{-2} radical contents of precipitation, which is subsequently the indication of SO_2 rise. Since some parts of gaseous SO_2 also dissolves in rainfall forming H_2SO_4. Out burst of population and industrialization are the main causes of air pollution. Rise in Cl/Na ratio supports the findings of earlier researcher[41], which state that there is possibility of supplemental sources of chloride ions present on the land.

WMO acid rain samples are laboratory simulated. It is seen that Cl/Na ratio is 1.66, *i.e.*, sea-water ratio (1.80) is nearly maintained in these samples.

Chembur shows the highest ratio of SO_4/Na – 9.18. Chembur is situated in the industrial belt and is highly polluted. SO_2 and related products are the main emissions of industries. As reported by Naik *et al.* (2002) non-sea salt SO_4 was found 97% at Chembur. The Chembur region accounts for over 50% of the SO_2 emitted by industries in Bombay.

6.   Ionic balance

Mean APWM in µeq/lit of major cations and anions are given in Table 3. The principle of electroneutrality in precipitation water requires that total anion equivalents equal total cation equivalents. (WMO 1994). Then only ionic balance is achieved. The ratio of major cations and anions (µeq/lit) is also given in the Table 3. This ratio (r) should be between 0.85 to 1.15, then only it is relevant. But it is seen that at Allahabad (r = 1.582) and Jodhpur (r = 2.11); this condition is not satisfied. This shows that there are some other anions, without accounting these ionic balance can not be achieved. These are most probably HCO_3^- ions. Carbonates and bicarbonates of

calcium and magnesium are available in abundance in Indian soil. Similar conclusions have earlier been drawn by Horvath and Meszaros (1984). In addition there are some organic acid ions (CH_3COO) also. The contribution of organic acids even for remote areas can be significant. Mohanbari, where vegetation cover is large, anthropogenic production of organic acids may be more to have significant contribution. However, organic acids only contribute the free acidity of rainfall at the time of collection and are consumed by microbes prior to analysis at central laboratories. Since our samples are analysed subsequently, the contribution of organic acids should be minimal. The high concentration of cations at Allahabad can be attributed to the erosion activity of the river Ganga which flows across the Himalayas and plains of U.P. This creates abundant soil derived water soluble aerosols, which are mostly alkaline (Ca, Mg, K) in nature. Jodhpur is located in desert area. Loose sandy soil, high temperature, dust storms and winds pump large amounts of soil derived alkaline aerosols in the atmosphere and less industrial development, low population prevent anthropogenic production of acidic aerosols. This is reflected in higher C/A ratio.

Ionic balance is achieved with acceptable range at Mohanbari and Nagpur acidic and alkaline pH data with C/A ratios – 0.98, 0.98, and 1.073 respectively. But at Chembur, even without considering NO_3 concentrations, C/A ratio is only 0.83. This clearly indicates that anions are present in such an excess quantity that cations are unable to neutralize them. Chembur is one of the highly polluted regions in Mumbai due to industrial activity.

7.   Conclusions

The studies of chemical composition of precipitation reveal the following conclusions :

(*i*)   Alkaline aerosols have more influence than acidic aerosols and are mainly responsible for high pH of rainfall in India.

(*ii*)   Soil derived aerosols of Ca and Mg which are alkaline in nature and present in abundance over Indian region control the acidification of rain over India.

(*iii*) Calcium is the most predominant cation and buffering element of Indian soil, while sodium is next to it and is of marine origin. Jodhpur has recorded the highest concentrations of both Ca and Na – 8.92 and 4.14 mg/lit (mean values).

(*iv*)   Sulphate and nitrate, the predominant anions next to chloride, show rise during the decade, with average nitrate levels higher than sulphate. These are mainly of gaseous

origin. Rise in these concentrations may be attributed to the industrialization and urbanization of the country.

(*v*) Mohanbari has recorded low pH values in acidic range throughout the decade. Lack of soil derived aerosols, which are the main buffering agents and excessive thunderstorm activity due to orographic features, in addition to fossil fuel combustion and oil refineries, may be responsible for low pH at Mohanbari.

(*vi*) Allahabad and Jodhpur are high pH regions (7.0). This can be attributed to the high quantities of soil derived alkaline aerosols available in the region as orographic features.

(*vii*) Nagpur has shown dual characteristic of pH – acidic and alkaline. But due to this random variation, the definite conclusions regarding the trend in pH can not be drawn, unless other met parameters like wind direction, wind speed, etc. are studied in detail.

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