Mausam, (1992), **43,** 3, 249-258

551. 577. 13 : 551. 510. 42 (540)

Precipitation chemistry over the Indian region

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(*Received 19 March 1991*)

सार — यह प्रस्तुत अध्ययन 1976-87 की अवधि के भारतीय क्षेत्र में पृष्ठभूमि वायु प्रदूषण मानीटरन संजाल (बेपमॉन) से लिए वृष्टि रसायन आंकड़ों पर आधारित है। ये प्रतिदर्श घटना के आधार पर बनाए गए हैं तथा वर्षा की समाप्ति के एकदम बाद प्रतिदर्शों के pH और विद्युत चालकता फिल्टिरित प्रतिदर्शों से निधारित किए गए हैं। मासिक मिश्र प्रतिदर्शों पर रसायनिक विश्लेषण किया गया है।

इलाहाबाद, पुणे और विशाखापट्टनम जो कि विस्तृत (मानवोद्भवी) प्रभावों के कारण क्षतिग्रस्त है, के अलावा पष्ठभूमि (बैकग्रांउड) क्षेत्रों से वर्षा जल के pH में कोई भी प्रवृत्ति नहीं पाई गई है pHSO$_4^{-2}$ आयन की तुलना में NO$_3^-$ आयन से अधिक सम्बद्ध प्रतीत होता है। नाइट्रेट के सान्द्रण में नियमित वृद्धि के होते हुए भी क्रमिक अम्लीकरण पर जांच रखते हुए अधिकांश स्थानों (मोहनबाड़ी के अलावा) पर क्षारीय मृदा व्यसन्न किस्मों के रूप में प्रकट होने वाले प्राकृतिक बफर समुचित प्रतीत होते है। HCO$_3^-$ की उपस्थिति को सम्मलित किए बिना आयन संतुलन प्राप्त नहीं किए जा सकते, ऐसी स्थिति वर्षा जल की प्रेक्षित विद्युत चालकता की व्याख्या करती है। भारतीय क्षेत्रों में समुद्री क्षेत्रों के लिए अम्ल एरोसॉलस् के साथ समुद्री एरोसॉलस के अन्तः सम्बन्ध का भी अध्ययन किया गया और समुद्र के नमक से क्लोराइड का पर्याप्त अभाव दर्शाता है। बेपमन आंकड़ों से NaCl के देशीय स्रोतों की भी पहचान कराता है।

ABSTRACT. The present study is based on the precipitation chemistry data from the Background Air Pollution Monitoring Network (BAPMoN) in the Indian region, for the period 1976-87. Sampling is made on an event basis and the pH and electrical conductivity of the samples are determined from filtered samples immediately after cessation of rain. The chemical analysis is performed on monthly mixed samples.

No trend is found in the pH of rainwater from background areas except at Allahabad, Pune and Visakhapatnam which suffer from sizable anthropogenic influences. The pH seems to be related more to NO_3^- ions compared to SO_4^{-2} ions. A natural buffer appearing in the form of alkaline soil-derived species seems adequate at most places (except Mohanbari), in keeping a check on progressive acidification despite steady increase in concentration of nitrates. The ion balance cannot be achieved without including the presence of HCO_3, which when done explains the observed electrical conductivity of rainwater. The interaction of marine aerosols with acid aerosols has also been studied for the marine regions in the Indian areas and reveals a substantial removal of chloride from sea-salt. Inland sources of NaCl have also been identified from the BAPMoN data.

Key words –Background Air Pollution Monitoring Network (BAPMoN), pH, Anthropogenic influences, Aerosols

1. Introduction

Ever since systematic analysis of rainwater was commenced in the decade of fifties (Barret and Bodin 1955, Junge and Werby 1958), the central objective of the Acid-Rain problem has been to identify the sources of the H^+ ion in rainwater. It is known that electrochemical considerations lead to a pH$\sim$5.65 for pure rainwater in equilibrium with atmospheric CO_2 gas (Erikson 1955). Therefore, it is natural to expect that with enhanced emissions of acidic gases due to industrialisation, the pH of rainwater should become further less. The phenomenon of gradual acidification due to rapidly rising SO_2 and NO_x levels was found particularly pronounced in Europe and America during the decade of the sixties (Likens and Borman 1974, Vermeulin 1980). In India, pH of rainwater was found to be in the range 6.0-7.1 as reported from the earliest measurements made by Mukherjee (1957) at the southern outskirts of Calcutta. The City being downwind of his experimental site his observations can be regarded as representative of background pollution. However, Handa (1969), noted a gradual lowering to a range of 5.8-6.3 in the same city. Infact even in the study of Mukherjee on one occasion when the prevalent wind was northerly the pH did register a downward dip. Data from other tropical areas for this period are scanty. Among a few significant studies is that of Visser (1961) from Uganda, reporting pH values as high as 5.9-9.5.

Alkaline components in soil derived aerosols, which are abundantly found in areas of dry convection due to intense insolation, coupled with lack of soil cover, give rise to higher pH in several areas of the tropical and sub-tropical regions. However, on downwind location of a city like Bombay, pH values of 4.5-5.2 are reported by Sequeira (1975) whereas simultaneous measurement at upwind sites revealed a pH of 6.1 to 6.3. It is, therefore, evident that the urban pollution does have the capacity to increase the hydrogen ion concentrations by one order or more over the background value.

It is now widely believed that neutralisation of acidic components in rainwater by calcarious aerosol species in the atmosphere acts as the main buffer mechanism against acid-rain (Krishna Nand 1984, Mukherjee *et al.* 1985, Khemani *et al.* 1985, Verma 1989). As a regional phenomenon, occurrence of acid-rain is virtually absent over the Indian region.

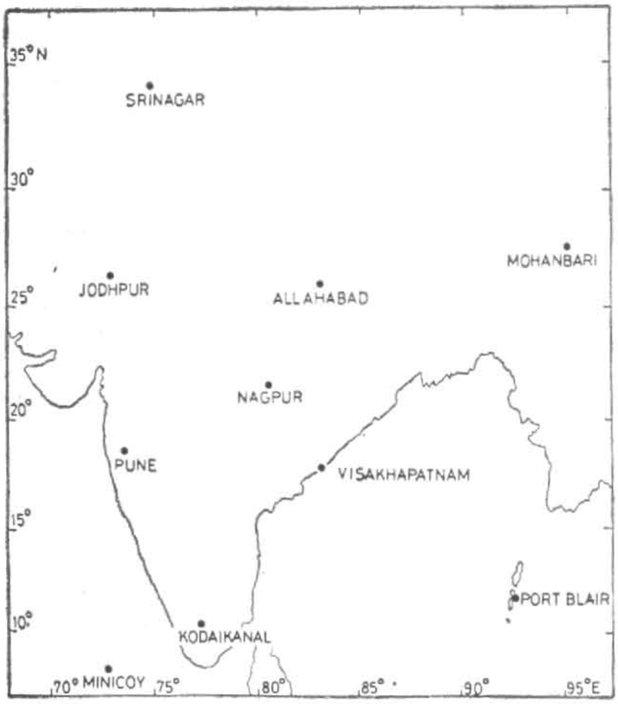


Fig. 1. Background air pollution monitoring network (BAPMoN) stations in India

In the present study, the precipitation chemistry data from the Indian Background Air Pollution Monitoring Network (BAPMoN) stations (Fig. 1), for the period 1973-1987, have been subjected to rigorous statistical analysis. The trends of pH values over the entire period for each station have been studied. The effect of quantity of rainfall has also been examined. A comparison of source characteristics of some important constituents have been made through a study of spatial distributions. The likely causes of variation of pH have been discussed for each station in detail.

1.1. *Methodology*

A wet-only sampling programme is undertaken at the ten BAPMoN stations, under the India Meteorological Department, using manually operated stainless steel collectors. Samples are filtered through Whatman-41 papers immediately after collection to remove any particulate matter. The pH and electrical conductivity are measured and then the sample is transferred to a polythene storage tank. Chemical analysis is done at the Central Laboratory at Pune on monthly-mixed samples for the ions, *viz.*, SO_4^{-2}, NO_3^-, Cl^-, NH_4^+, Ca^{+2} Mg^{+2}, $Na^+$and K^+. H^+ ion concentrations are measured using combination glass electrodes. Quality control in respect of contamination during handling is achieved through the consideration of conservation of electrical conductivity. Analytical reliability is checked by comparing measured and calculated electrical conductivity. The methods of chemical analysis are similar to that reported by Maske and Krishna Nand (1982). Analysis of samples collected beyond 1985, has been done on a Pye Unicam PU-9000 equipment. All the averages used in this study are precipitation volume-weighted means. This includes averages of pH also, which have been computed from the corresponding H^+ion concentrations.

2. Data summary and results

2.1. *The spatial variability of major constituents*

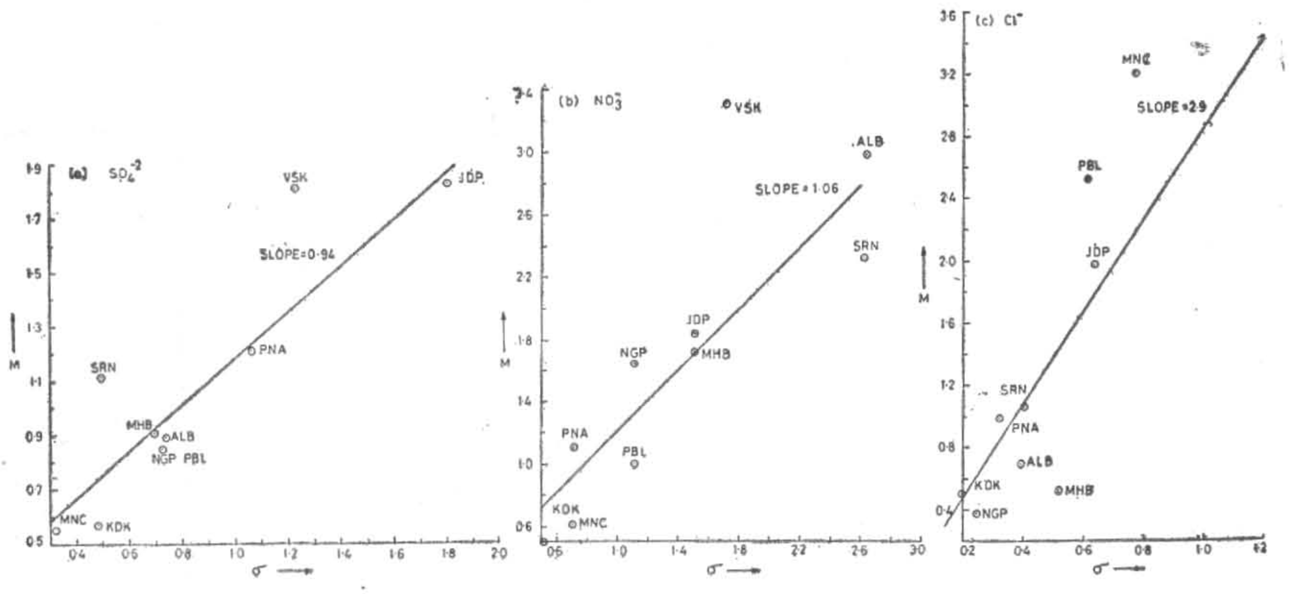
Table 1 gives the long term annual precipitation volume weighted means and standard deviations of concentrations of five important constituents of rain water, *viz.*, SO_4^{-2}, NO_3^-, Cl^-, Na^+ and Ca^{+2}. Large variability in all these constituents is noticed. The nitrate concentrations are generally larger than sulphate and chloride at all stations except at the coastal ones where the chlorides are either comparable or larger. Sodium content of coastal stations is also larger than the calcium content and for other stations it is the reverse.

Stations with very large calcium content are Jodhpur (desert) and Srinagar. Incidentally, Jodhpur also has the highest sulphate content and it may be noticed that it is the only inland station with very high sodium and chloride contents as well.

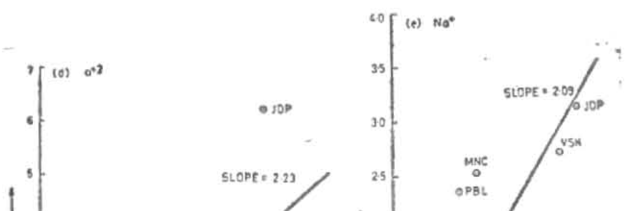
It is also interesting to note that Kodaikanal which is a high altitude station on a hill top, has the lowest concentration of all the species. At Port Blair and Mohanbari, concentrations are low on account of large number of rainy days and heavier rainfall that cuts off a large contribution of soil dust. To facilitate a comparison of total depositions, the mean annual rainfall of all the stations is also provided.

The dispersion characteristics of different ions present an interesting comparison. The coefficient of variation for Ca^{+2}, Na^+, K^+, and Cl^- are larger than those for SO_4^{-2}, NO_3^- ions. In some cases the standard deviations for Ca^{+2}, Na^+, K^+ and Cl^- are larger than those for other anions are comparable to their respective means. These populations are relatively flat and positively skewed, leading to large standard deviation values. It may be noted that the SO_4^{-2} and NO_3^- ions have gaseous sources also whereas the others come from particulate matter only. Dissolution of gases is a reverseable phenomenon and also depends on ambient concentrations which in any case are not high in background sites. That is why the mean values of SO_4^{-2} and NO_3^- concentrations are lower which bring down the average M/σ values in comparison to those of other ions.

The pictorial exposition of this is given in Fig. 2 (a-e). A majority of stations fit very well on the means versus standard deviation regression with the more powerful source regions for respective ions falling to the left of the lines.



Figs. 2 (a-c). Mean *vs* standard deviation of annual precipitation volume weighted means, at BAPMoN stations (1976-1987)



Figs. 2(d&e). Same as in Figs. 2(a-c)

2.2. *The trend of pH values of rainwater*

The interpretations of rainwater acidity determined by three different methods, *viz.*, pH sensing electrodes, titrations and Granats proposal are discussed by Tyree (1981). The results of different methods are rarely in agreement and not always reproducable. It may also be noted that rainwater contains both strong acids like H_2SO_4, HNO_3, HCl as well as the weak acids like H_2CO_3, CH_3COOH etc (Likens *et al.* 1976). In principle pH measurement alone cannot be considered adequate to explain the acidity or alkalinity of rain-water. However, at such extremely low concentrations as in the rain-water, both strong and weak acids are highly ionised and hence, the pH will be indicative of concentrations of strong and "some" of the weak acids. Moreover since these data are studied in conjunction with the results of chemical analysis, the exercise of ionic balance can lead to more reliable interpretations.

Fig. 3 shows the annual time series of pH data (1973-87). The long term mean values$\pm$standard deviation are printed on each diagram. The frequency distribution of the time intervals between extremes occuring in the time series suggests that a suitable filtration of short term fluctuations can be achieved using a two-year window for computing moving averages. The smoothened curves up to 1987 are depicted as dotted lines. Allahabad, Pune and Visakhapatnam show a significant downward trend (at 5% level). The epochal means for the block years prior to 1981 and subsequent to it, for these three stations, are also indicated. The time series has been extended to 1989 with recent data in the same figure.

The range of mean pH values occuring at all the stations is 6.28-7.42; the lowest value occuring at Mohanbari and highest at Jodhpur. There is a major downward gradient as one moves from the direction of west to east. The alkalinity drops with distance from the desert areas. However, Srinagar has a very high pH.

The weather systems affecting Srinagar are extra tropical in nature; the southwest monsoon which affects the rest of India does not reach there. Dust transported alongwith western disturbances co-occur with rainfall, thus causing this alkalinity.

2.3. *Variations with rainfall amount*

Linear regressions for monthly means of both pH and electrical conductivity with total rain amount for the month were computed. The results are given in Table 2. It may be noted that electrical conductivity is an indication of the total ionic concentration and thus represents the atmospheric load of both gaseous and particulate matter. Expectedly, the slope of the lines are all negative showing progressive increasing scavenging with higher rainfall amounts. The magnitude of the intercept decides the upper limit of the parameter

TABLE 1

Mean and standard deviation (1976-1987) of annual precipitation volume weighted concentrations (Unit :mg/lit)

Station	Elevation (m)	Location	No. of rainy days	Mean annual rainfall (mm)	SO_4^{-2}	NO_3^-	Cl^-	Ca^{+2}	Na^+
Allahabad	98	Continental, alluvial	53	1027	0.86 (0.72)	2.99 (2.63)	0.71 (0.38)	2.87 (1.35)	1.55 (0.62)
Jodhpur	217	Continental, arid	21	380	1.85 (1.80)	1.84 (1.67)	1.97 (0.62)	6.22 (1.70)	3.13 (1.30)
Kodaikanal	2343	Tropical, high altitude	107	1672	0.57 (0.48)	0.52 (0.5)	0.45 (0.22)	0.55 (0.47)	0.52 (0.33)
Minicoy	2	Arabian Sea, marine	94	1588	0.55 (0.32)	0.61 (0.90)	3.21 (0.75)	1.19 (0.27)	2.53 (0.63)
Mohanbari	111	Humid, alluvial	132	2759	0.91 (0.69)	1.75 (1.19)	0.53 (0.51)	0.57 (0.19)	0.59 (0.40)
Nagpur	310	Continental	60	1127	0.84 (0.72)	1.65 (1.14)	0.57 (0.23)	1.19 (0.40)	0.75 (0.40)
Port Blair	79	Bay of Bengal, marine	147	3180	0.84 (0.72)	1.01 (1.16)	2.53 (0.59)	0.62 (0.24)	2.33 (0.51)
Pune	659	Deccan Traps, semi-arid	50	714	1.21 (1.00)	1.71 (0.72)	0.99 (0.31)	1.29 (0.35)	0.87 (0.28)
Srinagar	1587	Extra-tropical, elevated valley	67	664	1.11 (0.99)	2.33 (2.61)	1.07 (0.39)	4.11 (2.27)	1.04 (0.24)
Visakhapatnam	72	Coastal	50	973	1.83 (1.22)	3.32 (1.72)	2.61 (1.17)	1.39 (0.40)	2.70 (1.25)

N.B. — The standard deviations are given in brackets

TABLE 2

Linear regressions of pH and electrical conductivity (μscm^{-1}) with rainfall amount (mm)

Station	pH		Mean pH	Elect. cond	
	M	C		M	C
Allahabad	—0.00340	7.31	7.23	—0.0462	42.6
Jodhpur	—0.00070	7.62	7.57	—0.1274	71.6
Kodaikanal	—0.00010	6.52	6.48	—0.0396	18.2
Minicoy	—0.00040	6.91	6.84	—0.0318	34.7
Mohanbari	+0.00030	6.22	6.28	—0.0135	26.9
Nagpur	+0.00005	6.48	6.49	—0.0387	23.2
Port Blair	+0.00118	5.93	6.29	—0.0166	29.8
Pune	+0.00082	6.75	6.80	—0.0735	38.8
Srinagar	—0.00139	7.50	7.41	—0.1143	66.8
Visakhapatnam	—0.00072	6.73	6.59	—0.1143	66.8

$Y = MX+C$, Y = pH/Elect. cond., X = Rainfall

obtained during the months when rainfall tends to zero. The high intercept values at Jodhpur, Visakhapatnam and Srinagar are in accordance with high values of average ionic concentrations as given in Table 1. It may be noted that Kodaikanal has the cleanest environment.

The relatively high values of slope at Jodhpur and Visakhapatnam are indicative of high washout efficiency. The washout efficiency is found to be a reflection of the total content of Cl^-, Ca^{+2} and Na^+, the three most electrically significant ions, that enter into rainwater. These ions enter into rainwater as a result of capture of dust and seaspray aerosols (both in the large size category *i.e.* ~ 1.0 μm) which is known to be more efficient than smaller particles or gases.

The interpretations of slopes for pH variation are not straight forward. All stations other than Mohanbari Nagpur, Port Blair and Pune show decreasing pH with increasing amounts of rainfall. Preferential removal of alkaline species or relatively higher presence of acidic precursors could explain this. Large atmospheric loads of calcarious crustal particles seem to be the principal factor that control the rainwater pH at these stations. On the other hand for the above 4 stations where pH shows an increase with rainfall, it is difficult to explain the increase of pH with rain amount. It would certainly be possible if soil dust itself has acidic constituents. Otherwise, transported anthropogenic contributions need to be considered. This aspect has been discussed in more detail in subsequent sections. However, it may be noticed that these stations, with the exception of Pune have slightly lower pH in general.

2.4. *Linear correlation coefficients with pH*

This hypothesis of the presence of H_2SO_4 and HNO_3 as principal acid components in rainwater can be tested using the model.

$$pH = A + B\ [SO_4^{-2}] + C\ [NO_3^-] \qquad (1)$$

TABLE 3

Linear correlation coefficients of pH with various factors
(C.C.=0.55 is significant at 5% level)

Station	Linear multiple correlation				Linear correlation coefficients				
	A	B	C	R^2	SO_4^{-2}	NO_3^-	Cl^-	Ca^{+2}	Mg^{+2}
Allahabad	6.20	2.85	−0.11	0.59	0.33	−0.51	0.24	0.57	−0.30
Jodhpur	7.56	0.13	−0.56	0.20	0.20	−0.25	0.06	0.30	0.65
Kodaikanal	6.07	6.69	−0.68	0.76	0.24	−0.65	−0.14	0.61	0.33
Minicoy	6.68	0.18	−0.07	0.00	0.04	0.02	−0.76	0.54	0.68
Mohanbari	6,28	−1.12	0.38	0.20	−0.36	0.14	0.03	−0.76	0.53
Nagpur	7.37	−1.13	0.07	0.52	−0.13	0.49	0.75	−0.46	0.42
Port Blair	6.15	1.09	−0.42	0.38	0.49	−0.49	0.02	−0.47	0.15
Pune	6.65	0.85	−1.42	0.56	0.49	−0.61	0.60	0.26	0.15
Srinagar	6.96	0.93	−0.14	0.31	0.31	−0.48	0.55	0.60	0.16
Visakhapatnam	6.25	0.32	−0.12	0.08	0.66	−0.12	−0.12	0.34	0.12

where the concentrations are in mg/lit. The role of SO_4^{-2} ions, in this model is slightly exaggerated considering that its equivalent weight is only 48 as compared to 64 of NO_3^- ion. In any case this difference is not significant considering the large unexplained variance in the observed data, by this model. However, the signs of B and C are important indicators. Vermeulin (1980), Fay *et al.* (1980) have also found poor correlations of pH with SO_4^{-2} and NO_3^- since these ions can have multiple sources in the form of mineral salts. Table 3 gives the linear multiple correlation coefficients of pH with respect of SO_4^{-2} and NO_3^- as well as simple linear correlation coefficients of pH with Cl^- and Ca^{+2}. The data are taken for monthly samples. Sodium is not considered since it is usually associated with neutral salts. Ammonium concentrations are extremely low and presumably, do not contribute significantly.

It may be seen that sulphates and nitrates combine to explain at best 76 per cent of pH variations at Kodaikanal. For Minicoy, they are insignificant and for other stations they are between 10-60 per cent. Negative correlations with NO_3^- are found for all station except Mohanbari and Nagpur where they show inverse correlation with SO_4^{-2}. It is thus possible that HNO_3 is a more common occurrence in rainwater in India. Minicoy is strikingly different from others in being influenced only by HCl. However, in the net ionic balance when equilibrium is reached all these acids stand neutralised.

Among the positive ions which substitute H^+ ions in equilibrium solutions to cause reduction in acidity, Ca^{+2} is found to be most important. It has positive correlations at Allahabad, Kodaikanal, Minicoy and Srinagar and slightly less at Visakhapatnam, Jodhpur and further less at Pune. At Mohanbari, Nagpur and Port Blair it assumes no role in neutralisation of acids, but its association with negative radicals needs to be determined to explain this aspect. It may also be remembered that these are among the stations where pH increases with rainfall. The lack of alkalinity from calcium, therefore, seems to indicate that the soils are not alkaline. The underlying presumption in these arguments is that the calcium comes from the soil, as discussed in the next section.

2.5. *Association between ions pairs and comparison with sea water ratios*

The association of Na^+ and Ca^{++} ions with various anions is determined from the values of linear correlation coefficients between monthly concentrations of the concerned pairs. Co-occurrence of Na^+ and Ca^{+2} ions is also tested in the same way. The results are given in Table 4. Ratios of SO_4^{-2}, Cl^-, Ca^{+2} and Mg^{+2} with Na^+ concentrations are given in Table 5. It may be noted that the ratios are for individual monthly samples and cannot, in principle, be compared to ratios computed from the values in Table 1.

(*i*) High correlation is obtained between Na^+ and Cl^- at all the island and coastal stations. Pune being closer to the sea also shows higher correlations. Here the correlation gets weaker when easterlies prevail over the station. Mohanbari also shows significant correlation and circulation features indicate substantial penetration of maritime air during the monsoon months (June-September). It is surprising that Jodhpur which receives maritime air after extensive travel over land should also show significant correlation, whereas other inland stations do not. The NaCl is most likely to be of local origin, as also indicated by high Na^+ to Ca^{+2} correlation. In fact, salt deposits due to evaporite formation in dry climate are known to exist near Jodhpur.

(*ii*) Substantial amounts of Ca^{+2} ions are derived from acidic mineral salts such as $CaSO_4$ at Allahabad, Minicoy and Visakhapatnam and $Ca(NO_3)_2$ at Mohanbari, Nagpur, Pune, Srinagar and Visakhapatnam

TABLE 4

Linear inter correlation between different ionic species
(Correlation coefficient = 0.55 is significant at 5% level)

Station	Ca^{+2} —SO_4^-	Ca^{+2} —NO_3^-	Ca^{+2} —Cl^-	Na^+ —SO_4^-	Na^+ —NO_3^-	Na^+ —Cl^-	Ca^{+2} —Na^+
Allahabad	0.56	0.19	0.21	0.28	0.21	0.65	0.20
Jodhpur	0.48	0.34	0.20	0.51	0.43	0.68	0.65
Kodaikanal	0.01	0.19	0.16	0.01	0.19	0.56	0.22
Minicoy	0.60	0.51	0.31	0.59	−0.10	0.80	0.48
Mohanbari	0.49	0.61	0.04	0.03	0.39	0.68	0.19
Nagpur	−0.23	0.68	0.58	−0.19	0.56	0.50	0.38
Port Blair	0.15	−0.02	0.42	−0.15	0.26	0.82	0.15
Pune	0.02	0.68	0.26	−0.10	0.19	0.68	0.22
Srinagar	0.32	0.69	0.48	0.37	0.66	0.46	0.36
Visakhapatnam	0.70	0.63	0.60	0.33	0.46	0.71	0.58

(*iii*) The ratios of concentrations of different ions with Na^+ when compared to sea water ratios indicate the strengths of continental sources. It may be seen from Table 5 that at all locations Ca^{+2} to Na^+ ratios are 1 to 2 orders higher than those for sea water and in view of the poor Ca^{+2} to Na^+ correlations, it is reasonable to infer that most of the Na^+ ions come from marine aerosols and the Ca^{+2} ions from the soil. The exceptions are Jodhpur and also probably Visakhapatnam. In the light of this it may thus be said that low Cl^- to Na^+ ratios compared to sea water indicate substantial loss of Cl^- ions from sea spray aerosols as they travel inland. The mechanism of this loss could be particulate phase NaCl reaction with free H^+ leading to formation to gaseous HCl (Erikson 1960).

Continental contributions of SO_4^{-2} ions seems to be high over Mohanbari, Pune and Nagpur and moderate over Srinagar and Kodaikanal. The sodium content being high for Jodhpur causes very low ratios at this station. At Minicoy, concentrations of SO_4^{-2} are extremely low and more linked with Ca^{+2} ions than Na^+ ions, causing low SO_4^{-2} to Na^+ ratio (Tables 1 and 4).

Mohanbari shows reasonably high Ca^{+2}/Na^+ values. But this excess calcium does not participate much in neutralisation of acidity. Its occurrence seems to be associated with nitrates and sulphates causing slight acidification instead. On the other hand, sulphates are also relatively in excess. Probably a part of these sulphates is associated with H^+ ions as shown by negative correlation with pH. This could also be the reason why Mohanbari has the lowest pH among other stations.

3. Discussion

The rainwater pH for the Indian background stations is in the weekly acidic to alkaline region. Poor correlations of anions with H^+ ion are attributed to neutralisation of strong acids by soil derived constituents; Calcium ions emerging among others, the most effective substitute for H^+ ions in equilibrium. In contrast to this lies the success of modelling pH using only SO_4^{-2} and NO_3^- concentrations for data from MAP-35 Precipitation Chemistry Network, in Northeast United States (Daniel 1981) and from the Canadian Network for Sampling Precipitation (Munger and Eisenreich 1983) and others. This is not surprising considering that Total Suspended Particulates (TSP) over these regions is only 20-60 $\mu g/m^3$ (WMO 1989) while that found in the north Indian plains are 100-200 $\mu g/m^3$ (Khemani *et al.* 1985) and from BAPMoN data, it is found to be around 200-800 $\mu g/m^3$ for Jodhpur and 50-200 $\mu g/m^3$ for Pune. Such high dust loads contain large quantities of minerals, some of which are hydrolised to weak acids while others are alkaline clay minerals and carbonates. Even a neutral salt like NaCl has a soil source, but only at one place, *i.e.*, Jodhpur where salt pans are found in some areas.

TABLE 5

Ratios of concentrations of SO_4^{-2}, Cl^- and Ca^{+2} with Na^+
(Concentrations are in units of mg/lit)

Station	SO_4^{-2}/Na^+	Cl^-/Na^+	Ca^{+2}/Na^+	Mg^{+2}/Na^+
Sea water	0.250	1.800	0.038	0.119
Allahabad	0.570	0.542	2.540	0.906
Jodhpur	0.456	1.581	3.543	1.303
Kodaikanal	1.056	0.918	0.945	0.311
Minicoy	0.360	1.063	0.684	0.351
Mohanbari	1.608	1.477	2.659	0.686
Nagpur	1.203	0.847	1.893	0.245
Port Blair	0.525	1.663	0.350	0.223
Pune	0.518	1.067	2.991	0.621
Srinagar	0.948	1.068	4.511	0.885
Visakhapatnam	0.603	1.277	0.810	0.501

It is, however, noticed that there is an alkaline dominance at most of the BAPMoN stations in India. Srinagar and Jodhpur may be classified as alkaline regions with Allahabad following closely. In all these stations there are large concentrations of calcium which are occasionally associated with SO_4^{-2} (mineral gypsum; acidic) and possibly with carbonates and bicarbonates (minerals, calcite, limestone and dolomite; alkaline). Handa (1969), Krishna Nand (1984), Mukherjee *et al.* (1985), Khemani *et al*, (1982) and Verma (1989) have reported the alkaline action of Ca^{+2}, but the possibility of its being otherwise is now noticed from the present study. Lower pH occurrence at Mohanbari, Port Blair and Visakhapatnam could not be explained earlier.

Mohanbari—The substantially excess Ca^{+2} as seen from the value of Ca^{+2}/Na^+ concentration ratio is to a large extent linked with $Ca(NO_3)_2$ and $CaSO_4$, both of which are acidic. The SO_4^{-2} concentrations are much greater than at other stations, which do not owe their origin exclusively to soil. Since the correlation of SO_4^{-2} with pH is negative, it is presumed that some H_2SO_4 must be also present in the atmosphere. The source of H_2SO_4 could be from SO_2 produced by flaring of natural gas in several oil wells in that area. The concentration of calcium is just sufficient to neutralise H_2SO_4. On certain occasions when the buffering is poor, the pH does come down sharply as seen in recent years (during 1988-89, a few monthly values have come down below 5.0).

Port Blair — In Port Blair Na^+ and Ca^{+2} are not associated with any acidic mineral salts, but the content of Ca^{+2} is extremely low. The SO_4^{-2} concentrations are also low on account of lower buffer content. However, sudden fluctuations to very low pH is not seen since there are no major anthropogenic pollution sources.

Nagpur —The Ca^{+2} in Nagpur appears to be associated with NO_3 and Cl^- to a great extent. Since concentrations are not particularly high, as compared to Jodhpur and Srinagar, the available Ca^{+2} in alkaline form is not high. On the other hand, SO_4^{-2} concentrations are substantially higher. These two factors result in an average pH of 6.50 at Nagpur. The absence of the sulphates (and also nitrates to a lesser extent) would have raised the mean pH to 7.37, as seen from the column A in Table 3. Such a clear dependence of pH on strong acid radicals is not seen anywhere else in the country. The source for this is likely to be emissions from coal fired Thermal Power Plants (2 MW capacity), which are situated about 25 km northeast of Nagpur. The effect is more pronounced in the winter season, when the winds are northeasterly. This also explains the positive slope of pH with rainfall, as seen in Table 2.

Visakhapatnam — Visakhapatnam shows occurrence of various mineral salts of marine as well as soil origin. Among them $CaSO_4$, $Ca(NO_3)_2$ account for substantial amounts of Ca^{+2} present in rainwater, thereby severely restricting its alkaline nature. It is quite probable that the cation exchange capacity of clay minerals which are predominant in montmorrilonite (Prakash Rao and Swamy 1987) causes the average pH to remain at around 6.60. But a lowering trend in annual pH is apparently due to anthropogenic emissions from the vehicular traffic in a growing city and from metallurgical industries situated to the northwest of the station.

Kodaikanal — Lower pH values are also reported at Kodaikanal. There is a strong influence of NO_3^-. The origin of NO_3^- is not likely to be any mineral salt, but could be a product of biogenic processes due to abundant vegetation at this high altitude tropical location. The Ca^{+2} available for alkalination is low because of the effect of altitude.

TABLE 6

Sulfur and nitrogen species concentrations from tropical regions

Station	Concentration, (μmolL^{-1})		Rainfall (mm/yr)
	SO_4^{-2}	NO_3^-	
Central Amazon	1.7	2.1	2400
Lago Calado, Brazil	1.9	3.5	2000
San Carlos, Venezuela	1.4	2.6	3910
Amazon Basin	4.4	2.1	2400
Katherine, Australia	—	4.3	1120
Katherine, Australia	2.0	4.9	1044
Jabiru, Australia	4.2	6.2	1568
Nigeria	4.0	—	860
Lamto, Ivory Coast	—	—	—
Lamto, Ivory Coast	16.0	—	687
Ayame, Ivory Coast	10.2	20.7	—

Reference Andreae *et al.* (1990)

It is interesting to compare depositions of SO_4^{-2} and NO_3^- over India with that of results from other tropical areas. Andreae *et al.* (1990) have stated values of SO_4^{-2} and NO_3^- concentrations in precipitation over tropical regions. They found that SO_4^{-2} concentrations over Central Amazonia during the wet season were extremely low and comparable with values reported for Antarctic ice, whereas the NO_3^- concentrations were relatively higher for the same area. They have also included values for other tropical regions which are reported from their work in Table 6. It may also be seen that both the NO_3^- and SO_4^{-2} concentrations over Ivory Coast are of the same order as over the Indian region. The SO_4^{-2} concentrations over Indian region are seen to be somewhat higher compared to those over other tropical regions and NO_3^- concentrations are seen to be substantially higher for Indian continental stations and not so for marine or hill stations.

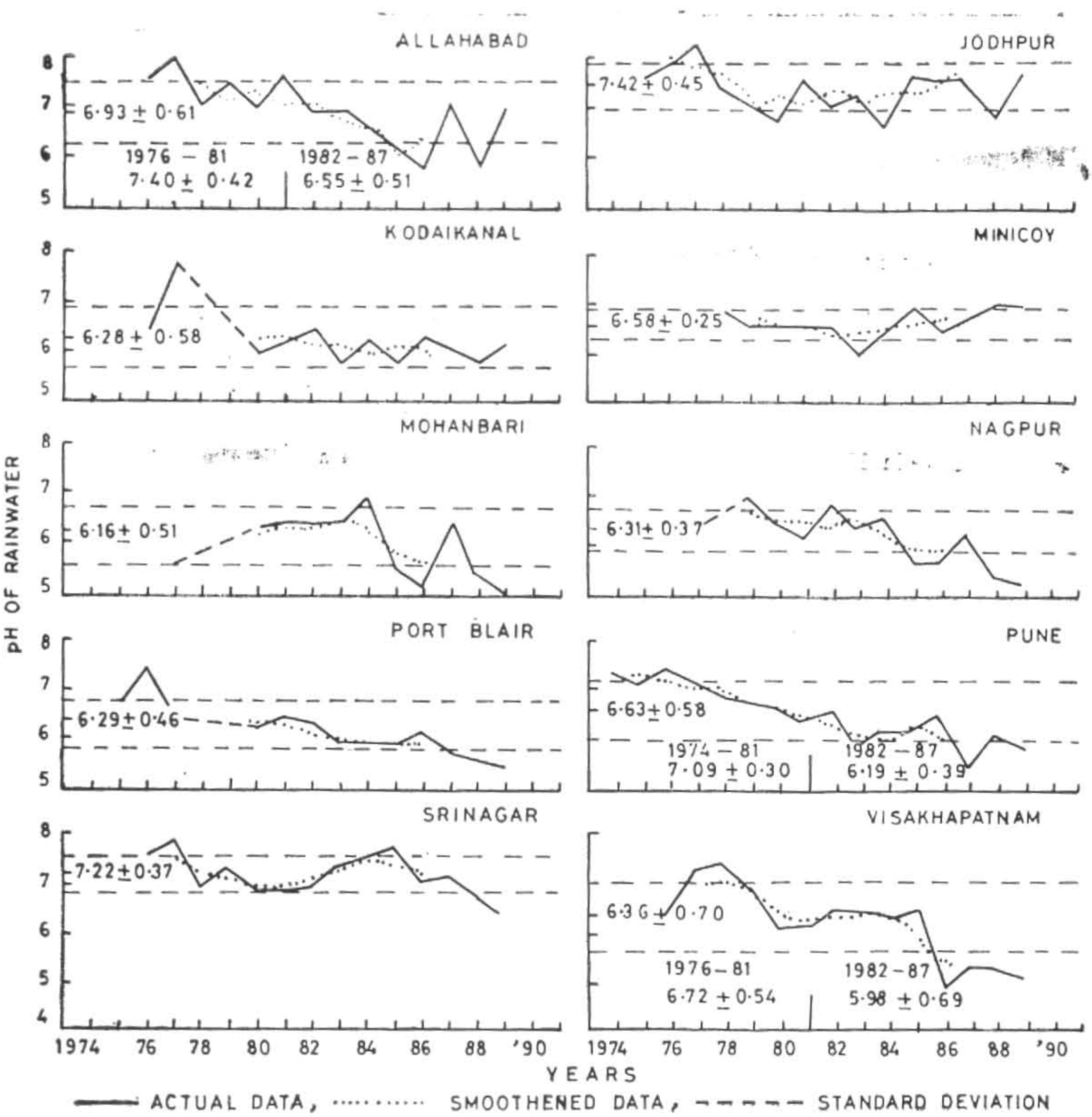


Fig. 3. Annual pH of rainwater in Indian BAPMoN stations

4. Ion balance and the need for a proxy ion (HCO_3^-)

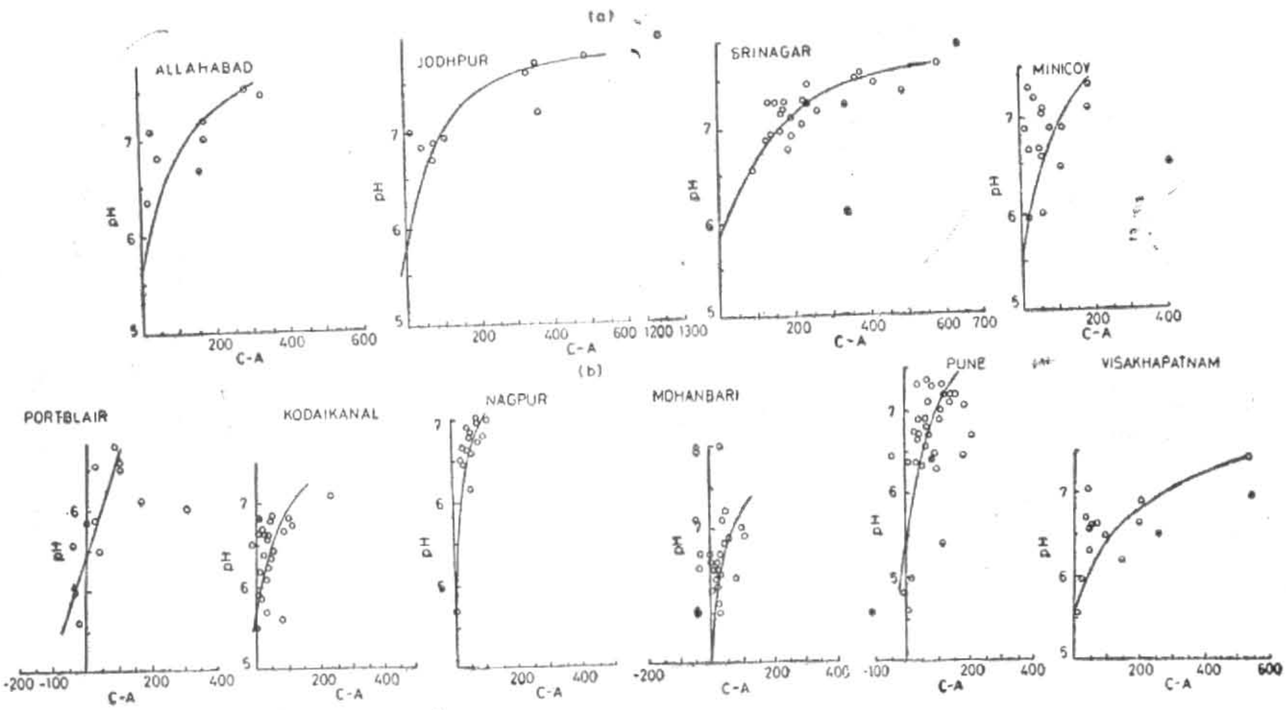
One reason for poor correlations between pH and the anions is that these form only about 50% of total anions. Ionic balance cannot be achieved in more than 95% of samples between Ca^{+2}, Mg^{+2} Na^+,K^+ and NH_4^+ denoted as C on one side and SO_4^{-2}, NO_3^- and Cl^- denoted as A on the other, when the concentrations are expressed in units of μeq/lit. H^+ion concentrations can never be expressed as $(C—A)$; this difference being always positive and in most cases large enough to be comparable to C. The following method was used to determine the missing ion :

$$C = \Sigma \, C_i, \qquad A = \Sigma \, A_j$$

$$L = \frac{1}{C-A}\left[E_m - \Sigma \, L_i \, C_i - \Sigma \, L_j \, A_j\right] \tag{2}$$

where L is the equivalent conductance of the unknown ion, E_m is the measured electrical conductivity in μ Scm $^{-1}$ and L_i, L_j are the equivalent conductances of various Ci and Aj.

The value of L was determined as the slope of the best fitted line between the numerator and denominator as appearing on the right hand side of Eqn. (2) above.



Figs. 4 (a & b). Dependance of pH on *C-A* (in μ eq/lit.) *C—A* presumed to be the bicarbonate concentration

It turned out that the proxy ion could be either HCO_3^- or CH_3COO^- or both. Organic acid radicals are expected to be low in background sites, except probably at Mohanbari and most of the values of *C—A* must be accounted for by HCO_3^-. Handa (1969) had earlier reported HCO_3^- concentrations in the range of 20-30 mg/lit from rain samples over Calcutta. This quantity should be more than enough to satisfy the requirement of *C—A* of our data. Linear correlation between the four metal cations and *C—A* show that significant correlation (at 5% level) exists with Ca^{+2} at Allahabad, Jodhpur, Mohanbari, Pune, Srinagar and Visakhapatnam, with Mg^{+2} at Allahabad, Jodhpur and Visakhapatnam and with K^+ only at Kodaikanal and Visakhapatnam. The source of $Ca(HCO_3)_2$ could be from fine clay size aerosol particles fractured from calcite and dolomite. The reaction being

$$CaCO_3 + CO_2(g) + H_2O \rightleftharpoons Ca\,(HCO_3)_2$$

It could also be formed as a result of cation exchange with clay minerals which have loosely bonded Ca^{+2} and Mg^{+2} and lend them to the water drops hydrating them at the expense of H^+ ions taken from them. The hydrogen ions may, in turn, come from the following reaction in rainwater :

$$H_2CO_3 \rightleftharpoons H^+ + HCO_3^-$$

implying that as more Ca^{+2} is released, more of HCO_3^- is formed. The latter reaction is more likely to explain HCO_3^- occurrence below 50 μeq/lit or so. The higher concentrations, therefore, must come from the earlier mechanism. The process of HCO_3^- formation is equivalent to that of removal of H^+ and to test this the plot of pH *versus* (*C-A*) was drawn [Figs. 4 (a&b)]. Lower pH regions shows a smaller range of (*C-A*) as at Mohanbari. The line is shown to pass through an intercept of pH=5.6; which would have been the theoretical value when (*C-A*) tends to the H^+ concentration.

5. Conclusions

The above study has brought out the following conclusions from the precipitation chemistry data of the Indian BAPMoN stations :

(*i*) Jodhpur, Srinagar and Allahabad are high pH regions (7.0). The higher pH is due to large quantities of soil derived aerosols which have Ca^{+2} and Mg^{+2} in the form of carbonates in addition to other mineral salts, some of which are weakly acidic also.

(*ii*) Mohanbari, Nagpur, Port Blair, Kodaikanal and Pune also have alkaline Ca^{+2} but to a lesser extent. Anthropogenic contributions in the form of acid precursors cause lowering of pH to a range of 6.4-6.8.

(*iii*) Minicoy falls in the intermediate category. NaCl in sea salt reacts with aerosol phase acids (H_2SO_4) and is probably a sink for the latter. Moreover, Mg^{+2}

is the dominant alkaline component. Its likely contributors are local soil and even possibly transported dust across Arabian Sea, supporting the results of Mukherjee *et al.* (1986).

(*iv*) The average levels of NO_3^- are larger han SO_4^{-2} at all background sites unless affected by higher ambient levels of SO_2 like at Mohanbari and Nagpur.

(*v*) In recent years Pune, Allahabad and Visakhapatnam have shown somewhat falling annual averages of pH. This is attributed to industrial pollution and could be linked with increasing NO_3^- concentrations.

Acknowledgement

The authors are thankful to the Director General of Meteorology, India Meteorological Department, for his encouragement.

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