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Long Term Variation in Precipitation Acidity over the Indian Global Atmosphere Watch (GAW) Stations

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Abstract: Acidic precipitation is a serious environmental hazard because of its capability of damaging environment worldwide. In this paper monthly variation and long term trend in pH, SO_4^{-2} and NO_3^- have been studied over a network of ten Global Atmosphere Watch (GAW) stations in India for the period from 1981 to 2002.

The analyses reveal that at Jodhpur and Allahabad precipitation is predominantly alkaline due to the influence of soil originated components derived from the Thar Desert and their transportation to these locations. Higher SO_4^{-2} and NO_3^- concentrations in precipitation at Visakhapatnam and Nagpur in most of the months in a year can be attributed to industrial and vehicular pollution. Higher concentrations of calcium, magnesium and potassium at Minicoy (Arabian Sea Island) cause its pH to be alkaline, whereas relatively lower concentrations of these basic cations at Portblair (Bay of Bengal Island) make its pH in the acidic range. During the period of 1981-2002, significant shift in pH towards the acidic range and increasing trend in sulphate and nitrate concentrations have been observed at most of the GAW stations. Further, decadal variations revealed drop in pH and substantial rise in sulphate and nitrate concentrations in 1991-2000 decade as compared to that in 1981-1990 decade at majority of the Indian GAW stations.

Key words: Acidic precipitation, pH, sulphate, nitrate, global atmosphere watch (GAW).

Introduction

Presence of high levels of acidity in rainwater, presumably from pristine tropical regions, has been observed by several authors (Galloway et al., 1982; Rao et al., 1995; Ayers et al., 2000). Galloway et al. (1982), analyzing precipitation chemistry data from the remote areas of the globe, recorded pH value of less than 5.0 in many of them (Amsterdam island in the Indian Ocean, 4.29, Alaska, 4.96, Katherine in Australia 4.78, San Carlos in Venezuela 4.81, Bermuda 4.79). Analysis of eastern U.S. precipitation data by Stensland and Semonin (1982) also indicated background pH values of around 5.0. However, in India some factors such as the presence of the Thar desert in the northwest, predominantly alkaline-rich soils, the sea and soil-derived aerosols in the coastal areas, tropical climatic conditions, low sulphur content in fuels coupled with the relatively low industrial growth are favourable in preventing acid rain problem in the country. Mukherjee and Krishnanand (1981) have shown that higher atmospheric temperatures in the tropics, lower solubility and dissolution rates of CO_2 added with rapid process of cloud formation and precipitation result in higher pH values. However, the current pace of industrialization and urbanization has overcome these favourable factors and as a result, most parts of the country are now showing drop in pH or acidic trends in the precipitation (Mohan and Kumar, 1998). The neutralization of acidic components in rainwater by calcareous aerosol species in the atmosphere act as main buffer mechanism against acid rain (Krishna Nand, 1984). Some parts of north-east and south-west India are classified as potentially sensitive to acidification due to low levels of prime acid neutralizers (Varma, 1989). The

lowering of pH in precipitation may take place in Asia in future due to the decrease in alkaline dust owing to mobilization and urbanization (Hedin et al., 1994).

A number of studies in precipitation chemistry based on long period data from Europe and USA reported significant decrease in SO_4^{-2} concentration along with increase in pH that could be directly linked to the decrease in emission of SO_2 (Puxbaum et al., 1998; Nilles and Conley, 2001). However, most of the studies show no significant trends for NO_3^-. Fujita et al. (2001) have reported substantial increase in NO_3^- concentration in precipitation at six rural stations in Western Japan during 1987-1996 and no significant change in the concentration of non-seasalt fraction of SO_4^{-2} was observed.

Systematic long term measurements of the chemical composition of precipitation from Indian region have been quite scanty. Khemani (1985) has reported decreasing trends in pH and other ionic constituents of rainfall at Pune except NO_3^-, Ca^{2+} and Na^+. Mukhopadhyay et al. (1992) have found a gradual increase in background levels of concentration of NO_3^- and H^+ in rainwater from Indian GAW stations during the period 1974-1991. Kumar et al. (2002) have reported chemical composition of monsoon rainwater collected at Dayalbagh for the year 1988, 1991-1996. The pH fluctuated between 6.7 and 7.07 and wind blown dust and soil played an important role in neutralizing precipitation acidity. Safai et al. (2004) studied chemical composition of precipitation at Pune for the period 1984-2002 and found gradual decreasing trend in pH mainly due to increasing SO_4^{-2} and NO_3^- concentrations. In a recent study, Sarkar and Soni (2006) assessed the balance between acidity and alkalinity at the Indian GAW stations by computing ratio of NP (neutralizing potential) to AP (acidifying potential). Their findings revealed that though the average value of NP/AP showed overall dominance of alkaline constituents that prevented acidification of rain water, yet the decreasing trend of this ratio, at most of the stations, indicated that the neutralizing capacity was decreasing.

With the increasing urbanization and industrialization the transport demand has increased substantially. The total number of vehicles in India has increased from about 5.3 million in 1981 to more than 53 million in 2000; with this has increased the vehicular pollution to a great extent. The power generating capacity in India has grown at rate of over 10% per year since 1950. Energy production in India mainly relies on coal which accounts for about 71% of the total. In this context power plants are the major sources of wet and dry deposition of sulfur since sulfur content in the coal used are found to range between 0.5 and 3%. The total Indian sulfur emissions due to large area and point sources are projected at 10,900 kt in 2010 and 18,500 kt in 2020 which are second largest in Asia, next only to China (Mohan and Kumar, 1998).

The India Meteorological Department maintains a network of Global Atmosphere Watch (GAW, formerly known as Background Air Pollution Monitoring Network) stations, which has the longest sampling record of precipitation in India. The present study reports a long term systematic study of precipitation acidity over a network of ten Global Atmosphere Watch stations (Figure 1) in India for the period from 1981 to 2002.

Figure 1: Indian global atmosphere watch network.

Methodology

A wet-only sampling programme was undertaken at the Indian GAW stations using manually operated precipitation collectors. pH value is measured at the stations after each event. Chemical analyses were done at the Central Laboratory at Pune on monthly mixed samples for the ions, viz. SO_4^{2-} and NO_3^-. The pH values were measured with a digital pH meter standardized with pH of 4.0, 7.0 and 9.2 reference buffers before pH determination. Atomic Absorption Spectrophotometric technique was used to measure cations Ca^{2+}, Mg^{2+}, Na^+ and K^+ and UV-Vis Spectrophotometric methods were used to determine SO_4^{2-}, NO_3^-, Cl^- and NH_4^+. 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. To exclude extreme outliers a simple statistical technique was adopted. Data points outside the range (m–3σ, m+3σ) were excluded, where m is the long term average and σ is the standard deviation. The

existence of a monotonic increasing or decreasing trend was tested with the nonparametric Mann-Kendall test.

Results and Discussion

Monthly Variation of pH Values

pH is an indicator of the intensity of acidity or alkalinity and measures the concentration of hydrogen ion in water. pH scale ranges from 0 -14 with 7 as neutral. The pH value lower than 7.0 refers to acidic solutions while higher than 7.0 value refers to basic ones, but for natural rainwater, in equilibrium with atmospheric CO_2, pH is 5.65; therefore, rainwater having pH value less than 5.65 is considered as acid rain.

Monthly mean values of pH at the Indian GAW stations have been presented in Table 1. At Jodhpur, Allahabad and Srinagar precipitation is predominantly alkaline in nature (monthly pH values are much higher than 5.65) which can be attributed to the influence of soil originated components derived from the adjacent Thar Desert. The dust transported along with western disturbances co-occur with rainfall at Srinagar thereby increasing alkalinity of rainfall. Calcium is found to be the predominant constituent in precipitation samples from Jodhpur (annual mean value 360.0 μeq l^{-1}) and Srinagar (annual mean value 280.7 μeq l^{-1}) with Allahabad (annual mean value 188.7 μeq l^{-1}) closely following (Figure 2).

At Mohanbari and Visakhapatnam, all the monthly mean values are acidic in nature. The concentration of SO_4^{-2} and NO_3^- at Mohanbari is lower than that at Allahabad, Jodhpur and Srinagar but the concentrations of soil originated components (Ca, Mg and K) in the precipitation is significantly less, because of which the pH of precipitation remains acidic. Vast area of North-east India is underlain by bedrock deficient in limestone and similar compounds needed to help neutralize or buffer the effects of acid precipitation. The region around Mohanbari is densely vegetated and soil is protected against wind erosion by vegetation. Presence of oil refineries, fertilizer factory, thermal power plant and oil and gas installations around Mohanbari are the chief contributors of SO_4^{-2} and NO_3^- concentrations. Thus Mohanbari has become vulnerable to acidic precipitation. Visakhapatnam is a coastal station and is also surrounded

Table 1: Particulars of Global Atmosphere Watch Stations in India and Monthly Mean pH Values (1981-2002)

Station Name (lat., long., alt.)	*Environment*	*Jan.*	*Feb.*	*Mar.*	*Apr.*	*May*	*June*	*July*	*Aug.*	*Sep.*	*Oct.*	*Nov.*	*Dec.*
Allahabad 25°27'N, 81°44'E, 98m	Mid-latitude, Continental and Urban	5.44	6.37	5.90	5.38	7.23	6.98	6.40	6.08	6.61	6.70	6.16	5.53
Jodhpur 26°18'N, 73°01'E, 217m	Mid-latitude, Arid and Urban	7.00	7.81	7.85	7.32	7.63	7.28	7.19	7.27	6.59	6.93	NR	NR
Kodaikanal 10°14'N, 77°28'E, 2343m	Tropical, High Altitude	6.29	5.60	5.50	5.96	5.49	5.45	6.21	5.67	6.06	5.60	5.72	5.75
Minicoy 08°18'N, 73°00'E, 2m	Tropical, Island in Arabian Sea, Natural	6.54	6.72	6.58	6.69	6.49	6.33	6.00	6.15	6.24	6.36	6.60	5.97
Mohanbari 27°29'N, 95°01'E, 111m	Tropical, Humid	4.52	4.59	4.71	4.55	5.03	5.36	5.41	5.27	4.72	4.78	4.73	5.09
Nagpur 21°06'N, 79°03'E, 310m	Continental, Urban	4.90	5.03	4.41	4.52	5.21	4.73	5.80	5.29	4.89	4.80	5.92	4.83
Portblair 11°40'N, 92°43'E, 79m	Tropical, Island in Bay of Bengal, Natural	4.85	4.70	4.95	5.43	5.35	5.28	5.33	5.85	5.69	5.33	5.58	5.53
Pune 18°32'N, 74°50'E, 559m	Continental, Deccan Traps, Semi-arid	6.50	5.65	NR	5.53	5.90	5.93	6.34	6.17	5.69	5.70	6.11	5.96
Srinagar 34°05'N, 74°50'E, 1587m	Extratropical, Elevated Valley	5.42	6.84	6.56	6.53	6.90	6.76	6.65	6.87	5.91	6.39	6.74	7.36
Visakhapatnam 17°41'N, 83°18'E, 72m	Tropical, Coastal Industrial and Urban	4.66	4.82	4.43	5.22	4.75	4.57	4.43	4.71	4.48	4.97	5.18	5.50

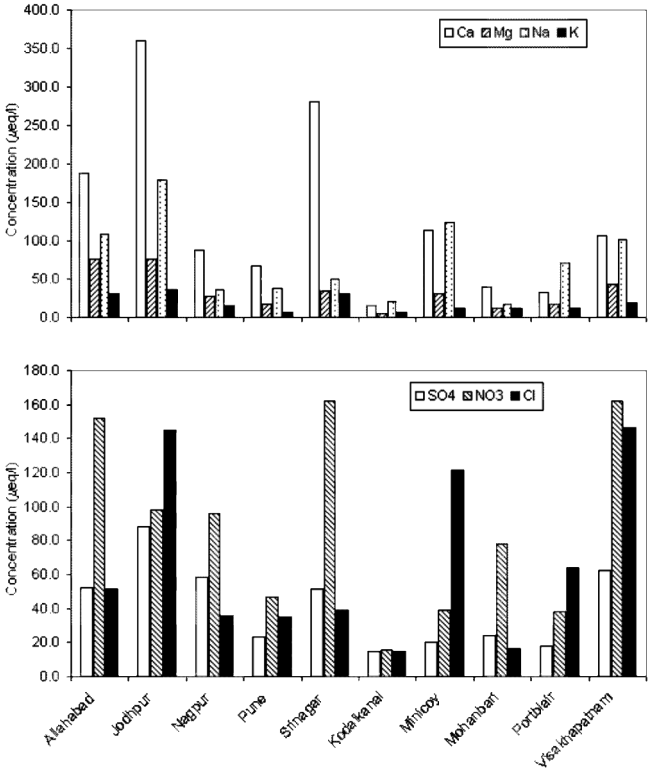

Figure 2: Long term mean value of concentration of cations and anions.

by fairly large number of industries including metallurgical industries, an oil refinery and a fertilizer factory. The composition of rainwater here also is influenced by pollution from local sources and sea spray thereby restricting the pH in the acidic range. At Nagpur, except two months, mean pH values are lower than 5.65. Anthropogenic emissions from vehicular pollution and coal fired thermal power plant situated about 25 km northwest of the station are the main reasons for acidic pH here.

At the two island stations of Minicoy (Arabian Sea) and Portblair (Bay of Bengal) picture is quite contrasting; at Minicoy all the monthly mean pH values are basic in nature. However, at Portblair, the values are acidic in most of the months. The concentrations of Ca, Mg and K in rainwater at Minicoy are quite high as compared to that at Portblair. Long-term mean values based on 1987-2002 data of Ca, Mg and K at Minicoy are found to be 113.8, 31.3 and 11.8 μeq l^{-1}, whereas for Portblair these values are 33.1, 16.7 and 11.3 μeq l^{-1} respectively. Consequently the pH values are higher at Minicoy as compared to those at Portblair. Khemani et al. (1985) also observed excess Ca in marine aerosol near the west coast of India over the Arabian Sea which is attributed to the transport of soil dust to the west coast of India from the Arabian Peninsula.

The precipitation at densely vegetated hill station of Kodaikanal is not only the least mineralized among all the other stations but also has low pH values. The high altitude at the mountain site reduces the amount of scavenging time of the rain. Also the vegetation around the site reduces the blowing of dust so that less neutralization occurs. There is strong influence of nitrate which could be a product of biogenic processes due to abundant vegetation around the station. The reason for low pH value in rainwater at Kodaikanal is not only the presence of acidic ions but also the low concentrations of soil originated components (Ca, Mg and K).

Long Term Trends in pH, Sulphate and Nitrate

Annual trend in pH, sulphate and nitrate at all the GAW stations have been presented in Figures 3a-b. Till the year 1980, pH values from the Indian GAW stations were around 7.0 or even higher (IMD, 1982). 1990 onwards, at majority of the GAW stations, pH values ranged between 5.0 and 6.0, indicating a shift from alkaline to acidic range. This change is attributed not only to increasing sulfate concentration, but even more to increasing nitrate concentration. Significant increasing trend (at 5% level of significance) in concentrations of SO_4^{2-} and NO_3^- and decreasing trend of pH is found at Allahabad, Kodaikanal, Mohanbari, Nagpur and Visakhapatnam. Jodhpur shows significant increasing trend in SO_4^{2-} but no significant trend in NO_3^- and pH. Although, the coastal station of Visakhapatnam shows considerable Cl^- concentrations, yet their effect on acidity is minimal because they are generally balanced by Na^+. Inter-annual fluctuations in ionic concentrations (SO_4^{2-}, NO_3^-) and pH are found to be substantial.

The overall time trends for pH are statistically non-significant for Minicoy and Portblair, but a slight decreasing tendency for pH is detected at both the places during the period of observation. The decrease in pH of rainfall at Minicoy and Portblair appears to be contributed by the observed increase of the nitrate and sulfate concentrations. The long term annual precipitation weighted mean data series from both the stations reveals an increasing trend in the concentration of sulfate and nitrate.

Some rain samples show sudden decrease in pH value. These are usually reported from Nagpur and Allahabad. They have been found to correlate very well with wind from large emission sources like thermal power plants. It is noted that the net cationic concentrations far outstrip net anions except Mohanbari. This is because of large

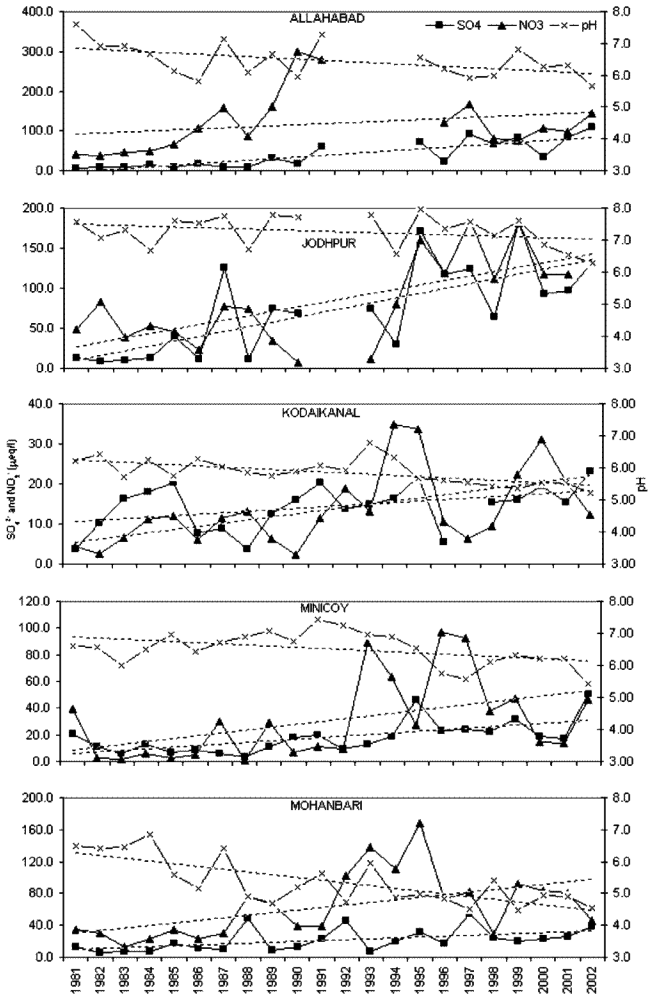

Figure 3a: Temporal variation of pH, SO_4^{2-} and NO_3^- at Indian GAW stations (1981-2002).

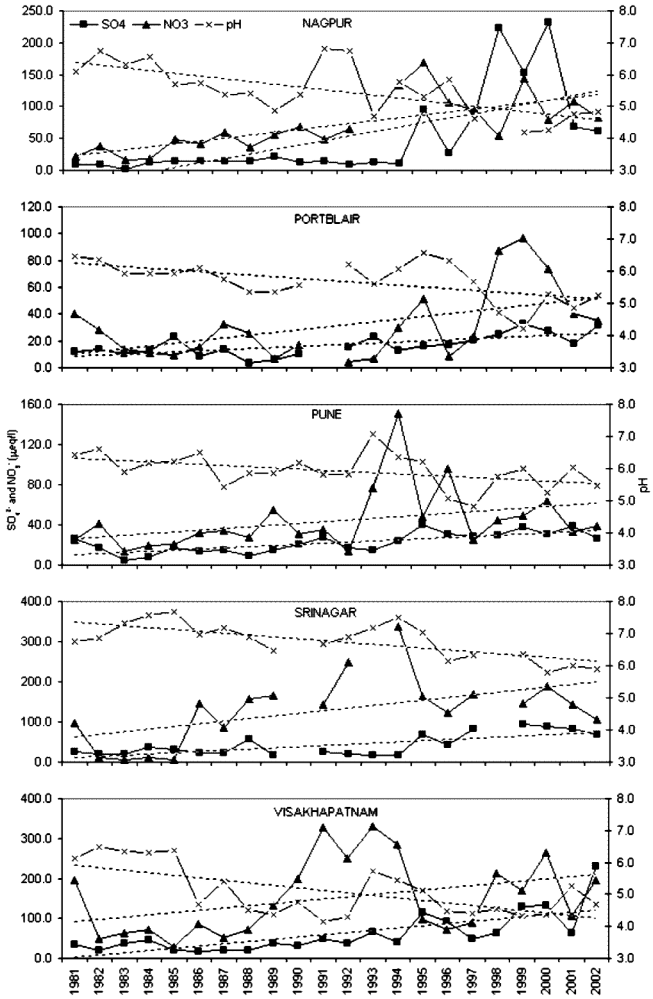

Figure 3b: Temporal variation of pH, SO_4^{2-} and NO_3^- at Indian GAW stations (1981-2002).

presence of HCO_3^- ions in rainwater which is usually not analyzed. The rainwater of the subtropical region that have one major rainy season, contains sizeable loads of HCO_3^- ions originating from soil in the form of soluble minerals and cation exchangeable clay minerals (Mukhopadhyay et al., 1992).

The concentrations of ions in rainwater at Pune show wide fluctuations because of the agriculture fields around the station which are fertilized with ammonium sulphate, sulphate of potash and urea etc. Along with the industrial growth in Pune during last few decades, there is a many fold increase in the industrial development in the region around Pune. Vehicular population has also increased drastically from two lakh in 1985 to more than 11 lakh vehicles in 2001. The pH is showing decreasing trend which can be attributed to increasing concentration of SO_4^{2-} and NO_3^-.

The precipitation weighted mean values of pH, sulphate and nitrate for the two decades 1981-1990 and 1991-2000 at the GAW stations have been presented in Figure 4. Comparing the shifts in the decadal means, it may be noticed that all the stations show a drop in pH in the later decade (1991-2000) except Jodhpur and Allahabad where the drop could be considered as nominal. The pH values at Srinagar and Minicoy were well within alkaline range during the decade 1981-1990, but in the later decade approximately 13% and 10% of the pH values are found to be in the acidic range respectively at these two stations. Except Kodaikanal, Minicoy, Portblair and Pune in rest of the GAW stations there is substantial rise in decadal mean values of sulphate and nitrate in 1991-2000 decade compared to that in 1981-1990 decade.

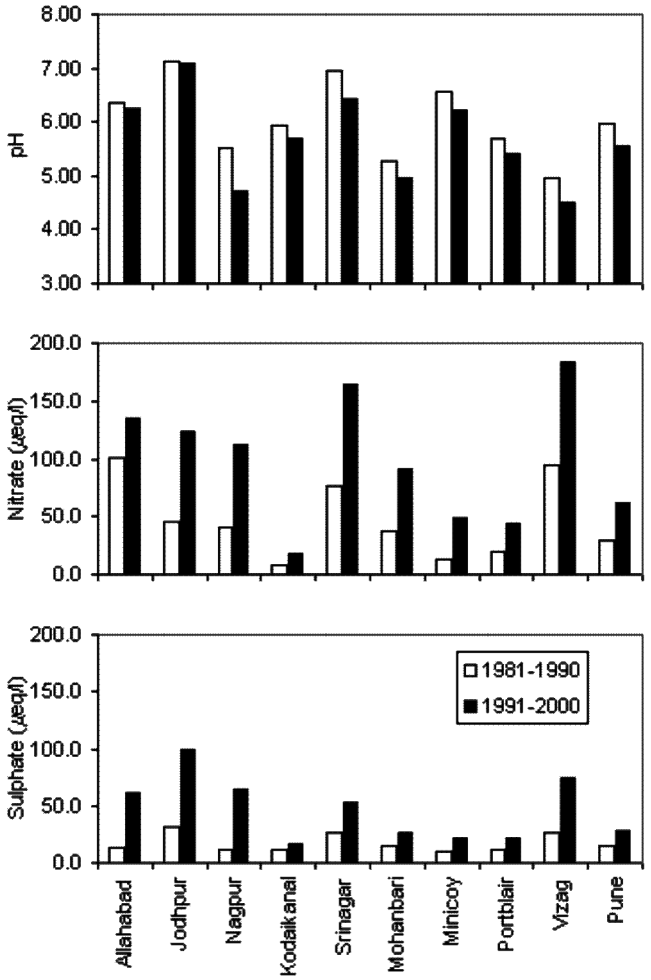

Figure 4: Decadal variation of pH, SO_4^{2-} and NO_3^-.

The mean values of NO_3^- ion concentration increased 1 to 1.7 fold in the later decade 1991-2000 at all the stations except Allahabad and Minicoy. At Allahabad the decadal rise is 0.3 times but Minicoy has shown a significant rise of 2.8 times. At Allahabad and Nagpur approximately four-fold rise is seen in decadal mean value of sulphate concentration while at Jodhpur and Visakhapatnam, the rise is almost two fold. The increase in mean concentration of sulphate is least at Kodaikanal, from 11.9 μeq/l in the decade 1981-1990 to 15.9 μeq/l in 1991-2000.

Conclusions

The geography and the climate have preserved India from an even higher acidity of rainwater than what actually occurred. The soil originated alkaline components play a major role in neutralizing acidity in rainwater in India.

At Jodhpur and Allahabad precipitation is predominantly in the alkaline range due to the influence of airborne particulate matters derived from the adjacent Thar Desert. The precipitation at Srinagar is also alkaline in nature mainly because of dust transport along with the western disturbances. At Visakhapatnam all the monthly mean (1981-2002) values and at Nagpur most of the monthly mean values are in acidic range, mainly due to higher sulphate and nitrate concentrations which can be attributed to industrial and vehicular pollution. Acidic precipitation at Mohanbari can be attributed to low concentration of soil originated components and high nitrate concentration.

Higher concentrations of calcium, magnesium and potassium at Minicoy (Arabian Sea Island) cause its pH to be alkaline, whereas relatively lower concentrations of these cations at Portblair (Bay of Bengal Island) make its pH in the acidic range.

During the entire study period (1981-2002), significant decreasing trend in pH and increasing trend in sulphate and nitrate concentrations have been observed at most of the GAW stations. Except Jodhpur and Allahabad, at the remaining GAW stations significant drop in decadal mean pH has been noticed in 1991-2000 decade compared to that in 1981-1990 decade. Substantial rise in sulphate and nitrate concentrations has been observed in 1991-2000 decade compared to that in 1981-1990 decade at all the GAW stations except Kodaikanal, Minicoy and Portblair.

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References

Ayers, G.P., Peng, L.C., Fook, L.S., Kong, C.W., Gillett, R.W. and P.C. Manins (2000). Atmospheric concentrations and deposition of oxidised sulfur and nitrogen species at Petaling Jaya, Malaysia, 1993-1998. *Tellus*, **52B(1):** 60-73.

Galloway, J.N., Likens, G.E., Keene, W.C. and J.M. Miller (1982). The composition of precipitation in remote areas of the world. *J. Geophys. Res.*, **89:** 1447-1458.

Hedin, L.O., Granat, L., Likens, G.E., Buishand, T.A., Galloway, J.N., Butler, T.J. and H. Rodhe (1994). Steep

decline in atmospheric base cations in regions of Europe and North America. *Nature*, **367:** 351-354.

IMD (1982). Atmospheric turbidity and precipitation chemistry data from Background Air Pollution Monitoring Network stations in India (1973-1980).

Khemani, L.T., Momin, G.A., Naik, M.S., Rao, P.S.P., Kumar, R. and Bh. V. Ramana Murthy (1985). Trace elements and sea salt aerosols over the sea areas around the Indian subcontinent. *Atm. Env*., **19:** 277-284.

Khemani, L.T. (1985). Characteristics of atmospheric gaseous and particulate pollutants and their influence on cloud microphysics and rain formation. Ph. D. Thesis, University of Poona.

Kumar, R., Rani, A., Singh, S.P., Kumari, K.M. and S.S. Srivastava (2002). A long term study on chemical composition of rainwater at Dayalbagh, a suburban site of semiarid region. *J. Atm. Chemistry*, **41:** 265-279.

Krishna Nand (1984). Prospects of acid rain over India. *Mausam*, **35(2):** 225-232.

Mohan, M. and Sanjay Kumar (1998). Review of acid rain potential in India: Future threats and remedial measures. *Current Science*, **75(6):** 579-593.

Mukherjee, A.K. and Krishnanand (1981). A physical reason for higher pH of tropical rainwater. *Mausam*, **32:** 231-236.

Mukhopadhyay, B., Datar, S.V. and H.N. Srivastava (1992). Precipitation chemistry over India. *Mausam*, **43(3):** 249-258.

Nilles, M.A. and B.E. Conley (2001). Changes in the chemistry of precipitation in the United States, 1981-1998. *Water, Air and Soil Pollution*, **130:** 409-414.

Puxbaum, H., Simeonov, V. and M.F. Kalina (1998). Ten years trends (1984-1993) in the precipitation chemistry in Central Austria. *Atm. Env*., **32:** 193-202.

Rao, P.S.P., Momin, G.A., Safai, P.D., Pillai, A.G. and L.T. Khemani (1995). Rainwater and throughfall chemistry in the Silent Valley forest in south India. *Atmos. Env*., **29(16):** 2025-2029.

Safai, P.D., Rao, P.S.P., Momin, G.A., Ali, K., Chate, D.M. and P.S. Praveen (2004). Chemical composition of precipitation during 1984-2002 at Pune, India. *Atmos. Env*., **38:** 1705-1714.

Sarkar, Jayanta and V.K. Soni (2006). Are acid rain phenomena at the Indian WMO/GAW (Global Atmosphere Watch) stations showing upward trend? Paper presented at the International Conference on Mesoscale processes in atmosphere, ocean and environmental systems, held at Indian Institute of Technology, Delhi, India, 14-17 Feb., 2006.

Stensland, G.J. and R.G. Semonin (1982). Another interpretation of the pH trend in the United States. *Bull. Am. Meteorol. Soc*., **63:** 1277-1284.

Varma, G.S. (1989). Background trends of pH of precipitation over India. *Atmos. Env*., **23(4):** 747-751.