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MAJOR INORGANIC ION COMPOSITION OF RAINWATER AT SOME GAW (BAPMoN) STATIONS IN INDIA

1. Air pollution has become worldwide problem during last few decades. Alarming levels of air pollution are a serious threat to human life and property. In addition to this a precise knowledge of chemical composition of the atmosphere is important to study the phenomenon of climate change. Chemical analysis of precipitation is a very useful tool since most of the water soluble pollutants are removed by rain.

In India ten stations have been established in 1973 under WMO project named Background Air Pollution Monitoring Network (BAPMoN), now known as GAW (Global Atmosphere Watch). Wooden precipitation collectors, specially designed and developed, as per WMO (BAPMoN), recommendations have been installed at all ten GAW stations. Shower wise rainfall samples are collected in polyethylene bottles at these stations. These samples are then transferred to bigger container and monthly mixed rainfall sample is sent to the Air Pollution Section in the office of A.D.G.M.(R) Pune for further analysis.

Such rainfall samples received from all ten stations are analysed regularly at Pune Laboratory to determine concentration (reported in mg/lit) of various cations and anions. Atomic Absorption Spectrophotometer is used to determine the concentration of cations (Ca, Na, Mg & K) and UV-Visible Spectrophotometer for anions $\left(Cl^{-}, SO_4^{-2} \,\&\, NO_3^{-1}\right)$, and NH_4^{+}. Earlier Maske and Krishna Nand (1982) reported that the Bay of Bengal and the Arabian Sea are the major sources of Chloride and Sodium in rainwater samples. Krishna Nand (1984), Mukherjee *et al.* (1985) and Khemani *et al*. (1985) pointed out that Calcarious aerosol species in the atmosphere act as the main buffer mechanism against acid rain. Mukhopadhyay *et al*. (1992) observed that SO_4^{-2} concentrations over Indian region are higher as compared to those over other tropical regions and NO_3^{-} concentrations are seen to be substantially higher for Indian continental stations than marine or hill stations.

In the recent studies Momin *et al*., (1999) studied chemical composition of aerosols at Thiruvananthapuram and Pune and observed that cations dominated anions at both the places indicating alkaline dominance over the continent.

The objective of present studies is to find out variations in the concentrations of chemical constituents of precipitation at different locations, climatic conditions. For this purpose chemical composition data of precipitation at Allahabad (Lat. 25° 27' N, Long. 81° 44' E) and Kodaikanal (Lat. 10° 14' N, Long. 77° 28' E) situated at different climatic conditions for the period 1988- 97 have been considered.

2. Two stations selected for the studies are situated at totally different climatic conditions - Allahabad -continental, alluvial soil while Kodaikanal - tropical high altitude. APWM values of all water soluble constituents for Allahabad for the period 1988-97 are plotted in Fig. 1. Similar data for Kodaikanal are plotted in Fig. 2. It is seen that at Allahabad, concentration of all cations except Ca^{+2}, shows a falling trend. Ca^{+2} concentration shows a very little rise. On the other hand, SO_4 concentration shows a continuous rise throughout the decade. This can be attributed to the industrial growth. Cl and NO_3 concentrations show falling trend but in NO_3 concentration, the fall is negligible. At Kodaikanal, all APWM values are very low indicating less pollution. Ca^{+2} and Mg^{+2} concentrations show a rising trend. Na^{+} and K^{+} alongwith Cl^{-} and NH_4^{+} show a falling tend. But fall in Na^{+} and NH_4^{+} is very little. SO_4 and NO_3 show a rising trend, though NO_3 shows fall and SO_4 a sudden rise after 1996. The increasing trend of cations and decreasing trend of anions indicate less industrial development/urbanisation and clean atmosphere at Kodaikanal.

2.1. Table 1 gives mean (APWM) concentration values (mg/lit) of major water soluble constituents and standard deviations. It is seen that mean concentration and S.D., both values are very high at Allahabad than at Kodaikanal as expected. In addition individual constituents also show higher variability at Allahabad than at Kodaikanal. The lowest concentration at Allahabad is that of NH_4^{+} (0.25 mg/lit) and the highest is of NO_3 (11.43 mg/lit), while at Kodaikanal these are Mg (0.06 mg/lit) and NO_3 (1.23 mg/lit) respectively. It is noticed that NO_3 concentration is the highest at both the stations, but at Allahabad it is 10 times higher than that of Kodaikanal. This may be due the virtue of the orographic features where the stations are located as well as industrial develpoment at Allahabad.

The mean concentrations of cations –Na, Ca, Mg & K are higher than those of Cl & SO_4 at Allahabad. This is reflected in the mean pH value which is higher

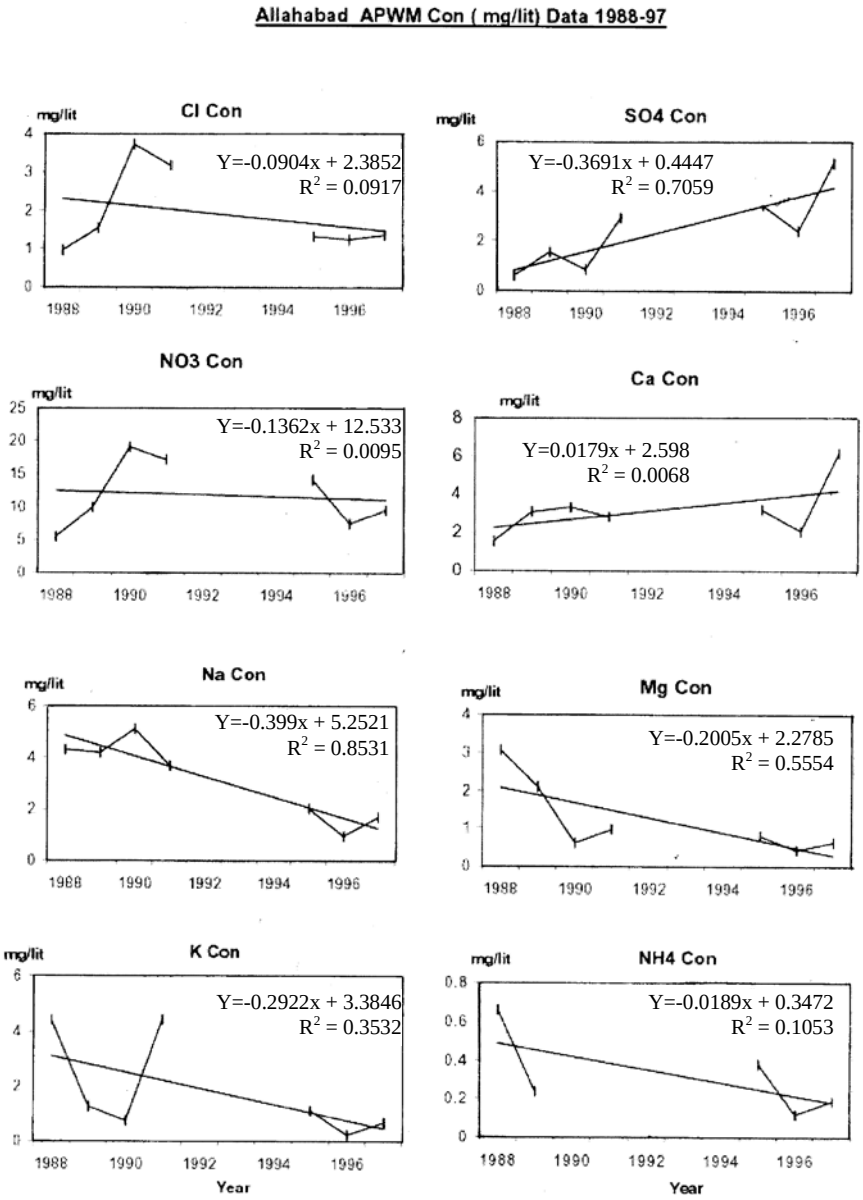

Fig. 1. APWM values of water soluble constituents for Allahabad for the period 1988-97

at Allahabad (6.14) than at Kodaikanal (5.90). The alkaline constituents of soil derived aerosols are mainly responsible in neutralising acidic components in precipitation. (Krishna Nand 1984, Mukherjee *et al*. 1985, Khemani *et al*. 1985). This also indicates abundance of alkaline aerosols in the atmosphere at Allahabad than at Kodaikanal.

3. Kodaikanal is situated at an elevation of 2343 mts asl on the top of hills – Nilgiries. The station gets rainfall from both SW & NE monsoons and hence most of the year rainy weather prevails over the city. Due to hilly orography and high altitude there is very little industrial development and hence less pollution. This is very well reflected in the chemical composition of the precipitation. The concentration of all constituents remains much lower. Due to damp, cloudy weather very less soil derived aerosols are available in the atmosphere. Less industrial development controls pumping of industrially derived aerosols, which are mostly acidic, in the atmosphere. This maintains high pH values of rainfall (mean 5.90), which are well within alkaline range, with a few exceptions in marginally acidic range. NO_3^- and SO_4^{-2} values (mg/lit) show rise from 1993 onwards.

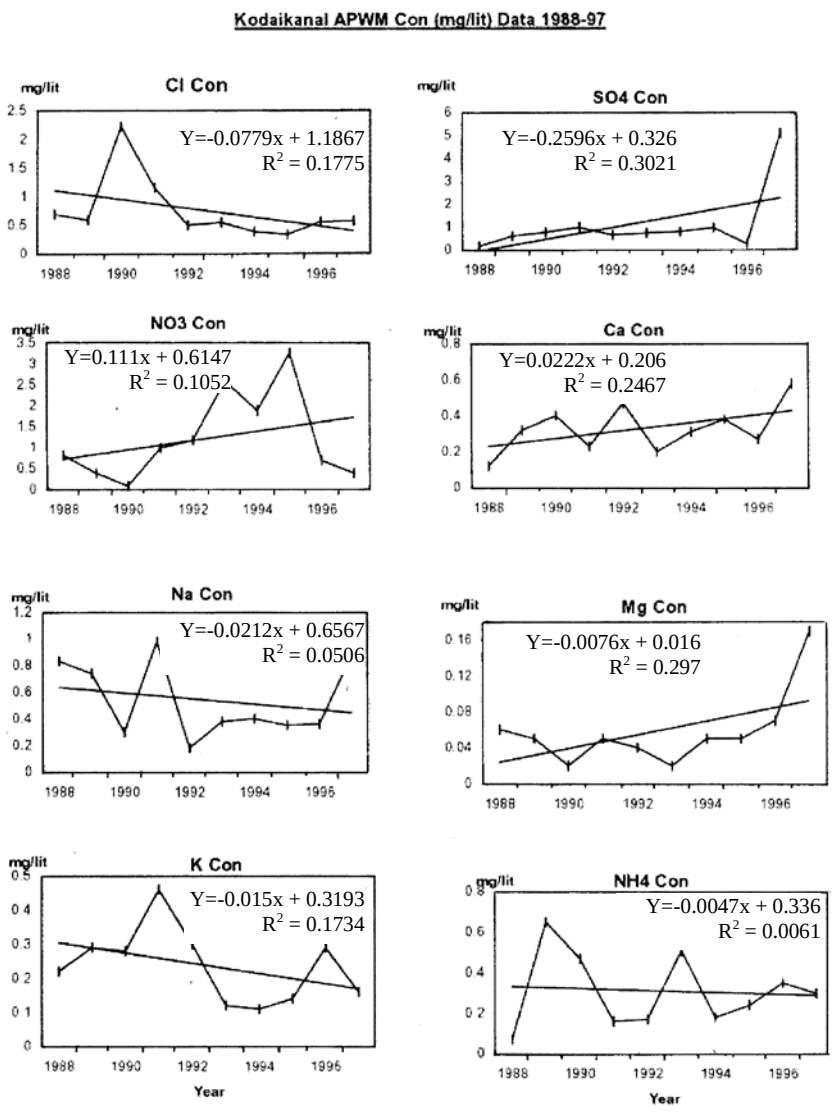

Fig. 2. APWM values of water soluble constituents for Kodaikanal for the period 1988-97

At Kodaikanal, only January, February and December-to some extent-get less rain as compared to other months. Hence during these months, the concentration of all constituents-cations and anions is higher as compared to monsoon months June to September as expected. This is the wash-out effect of precipitation, which removes most of the water soluble particulate matter.

3.1. Allahabad is surrounded by many small scale industries and sugar factories. These are the main sources of pollution of all kinds – aerosol particulate matter, gaseous emissions, anthropogenic productions etc. This is reflected in the higher concentration of NO_3^- and SO_4^{-2}. The city experiences very high temperatures - upto 45 °C - during summer months. Convective activity and dust raising winds pump soil derived aerosols in the atmosphere, rainfall activity is restricted to monsoon season only. Hence concentration of all chemical constituents show fall during the monsoon months as compared to other months, maintaining seasonal trend.

3.2 It is seen from Table 1, that Ca^{+2} is the most predominent cation with mean concentration of 3.18 mg/lit and Na is the next one with mean concentration of 3.14 mg/lit at Allahabad. Handa (1969), has reported same findings of Ca^{+2} dominance over Calcutta. Earlier studies carried out by the author also indicate dominance of Ca^{+2} at other network stations, Shende, (2001). But at Kodaikanal, Na shows higher concentration (0.54 mg/lit)

TABLE 1

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

Chemical	Allahabad			Kodaikanal		
constituent	Mean	S.D.	μeq/lit	Mean	S.D.	μeq/lit
Na	3.14	1.57	136.58	0.54	0.28	23.49
Ca	3.18	1.47	155.88	0.33	0.13	16.46
Mg	1.29	1.14	106.17	0.06	0.04	4.93
NH_4	0.25	0.21	13.13	0.31	0.18	17.18
K	1.84	1.79	47.06	0.24	0.11	6.14
Cl	1.91	1.09	55.43	0.76	0.56	22.05
SO_4	2.40	1.60	49.97	1.10	1.43	22.90
NO_3	11.43	5.47	178.57	1.23	1.03	19.21
pH	6.14	0.67	0.72	5.90	0.40	1.24
Total cations			459.54			69.44
Total anions			283.97			64.16
A:C Ratio			0.62			0.92

than that of Ca^{+2} (0.33 mg/lit). Same is the case with Cl concentration, which is lower (1.91 mg/lit) than Na concentration (3.14 mg/lit) at Allahabad, but higher (0.76 mg/lit) than Na concentration (0.54 mg/lit) at Kodaikanal. This can be attributed to monsoon effect, which prevails over Kodaikanal , most of the year. The winds coming over the Arabian Sea and the Bay of Bengal bring sea-spray aerosols containing Na & Cl radicals. Also there is very little chance for soil derived aerosols due to cloudy weather. But at Allahabad higher concentration of Na indicate availability of another source of Na radical. This may be anthropogenic or soil derived.

Abundance of K and Mg particles is also seen at Allahabad with mean concentration 1.84 mg/lit and 1.29 mg/lit respectively, than that of Kodaikanal which shows the lowest concentrations of K (0.24 mg/lit) and Mg (0.06 mg/lit). Potassium (K) particles are mainly of land origin. Higher concentrations of K & Na particles at Allahabad may be due to excessive use of fertilizers containing these radicals. Phosphates and sulphates of potassium and sodium are the popular fertilizers used for sugarcane crops.

3.3. During 1979, concentrations of Sulphate and Nitrate were lower than concentration of Chloride at all BAPMoN stations, (Maske & Krishna Nand, 1982). But, the present study reveals that the concentration of NO_3 is the highest at both the stations and concentration of Cl is the lowest one, with the concentration of SO_4 in between, (Table 3). This is the indication of increasing level of pollution which has reversed the order of concentrations.

TABLE 2

Ratios of various chemical constituents with Na (by weight)

	Sea water	Allahabad	Kodaikanal
C1/Na	1.8	0.61	1.41
SO_4 /Na	0.25	0.76	2.04
Ca/Na	0.38	1.01	0.61
Mg/Na	0.12	0.41	1.07
K/Na	0.36	0.59	0.44

3.4. Ratios of various chemical constituents of precipitation with Na by weight have been calculated and given in Table 2. This helps in determining the strength of continental sources and also to some extent level of pollution. Deviation of these ratios from that of sea-water ratios indicates availability of either of the ions in excess quantity or loss due to some reason. This ratios of various species are lower at Allahabad as compared to the same ratios at Kodaikanal. Only Ca/Na ratio is higher (1.01 mg/lit) than at Kodaikanal (0.61 mg/lit). This indicates availability of ample calcium salts in the soil of Allahabad. Mukhopadhyay *et al.* (1992) have also reported higher ratios of Ca/Na. These are mostly sulphates (Gypsum - acidic), carbonates and bicarbonates (minerals, calcite, lime-stone and dolomite - alkaline). Low ratio of Cl/Na (0.61) at Allahabad is quite in agreement with earlier studies indicating loss of Cl ions

TABLE 3

Correlation co-efficient (*r*) between ionic species

Species	Allahabad	Species	Kodaikanal
Na : Cl	0.71	K: Cl	0.48
Na : SO_4	0.31	NO_3 : Ca	0.47
Na : Ca	0.36	K: Na	0.35
Cl : SO_4	0.40	Cl : Ca	0.15
K: Cl	0.54	Cl : Na	0.63
K: NH_4	0.17	SO_4 :Na	0.29
Ca : Mg	0.27	Mg : Na	0.21

from sea aerosols as they travel in land (Eriksson 1960). This is also supported by higher Cl/Na ratio (1.41) at Kodaikanal which is situated at nearer distance from both the Arabian Sea and the Bay of Bengal. Higher ratios of Cl/Na (1.41), SO_4/Na (2.04) and Mg/Na (1.07) at Kodaikanal are also indicative of less availability of soil crust / aerosols containing sodium compounds.

3.5. Coefficients of correlation of monthly rainfall samples have been calculated with various species to find out association between cations and anions. (Table 3). High correlation between Na and Cl at both the stations, Allahabad (0.71) and Kodaikanal (0.63) indicate the influence of sea-spray aerosols of NaCl at both the places. K & Cl radicals also show high association ALB (0.54), KDK (0.48) next to Na & Cl. With high concentration NO_3 and SO_4 show very poor association with other cations. This shows that these radicals may be the result of vehicular exhaust of trucks used in the industrial activities and emissions from diesel pumps used for crop irrigation, which contain nitrogen oxides (NO, NO_2).

The ratio of major anions and caions at Allahabad is 0.62 and at Kodaikanal is 0.92 , (Table 1). The low ratio at Allahabad indicates that ionic balance cannot be explained without considering weak acid ions like HCO_3^-. This is quite in agreement with the hypothesis quoted by Mukhopadhyay *et al*. (1992). This higher 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 creats abundant soil derived water soluble aerosols, which are mostly alkaline (Ca, Mg) in nature. This may also be the reason for higher pH (mean 6.14) at Allahabad.

Ionic balance at Kodaikanal is very well established with ratio value of 0.92. Hilly orography, hard rock soil, high elevations and typical rainy, cloudy, damp weather give very little room for soil derived aerosols and less industrial development arrests input of NO_X (NO_3), SO_2 (SO_4) radicals from vehicular exhausts into the atmosphere. This is reflected in pH value also, which is (mean 5.90) lower than that of Allahabad (mean 6.14).

4. Chemical analysis of rainfall samples at Allahabad and Kodaikanal reveals following conclusions :

(*i*) Alkaline aerosols have more influence than acidic aerosols at both the places. This is reflected in pH values which are well within alkaline range at both the places.

(*ii*) High concentrations of NO_3^- (11.43 mg/lit) and poor correlation with cations at Allahabad indicate that the local sources like vehicular and other low quality diesel driven machine (pumps) exhausts (emissions) may be responsible for high level of NO_3.

(*iii*) Higher values of sulphates and nitrates at Allahabad indicate that local sources are responsible for affecting the pollution level at Allahabad.

(*iv*) Sodium and Calcium are the predominent cation while chloride is the predominent anion next to sulphate and nitrate at both the places.

(*v*) The Arabian Sea and Bay of Bengal are the major sources of sodium and chloride in precipitation.

(*vi*) Well established ionic balance with low concentrations of major constituents at Kodaikanal indicated that climatic conditions and industrial development are the main deciding factors of pollution at a particular place.

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