Study of chemical species in rainwater at Ballia, a rural environment in eastern Uttar Pradesh, India

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Samples of rainwater were collected at a rural environment in eastern Uttar Pradesh at Ballia using 24-h sampling period from July to September 2001. Bulk collector was used for collection of rainwater. All samples were analyzed for major ions (Cl^-, SO_4^{2-}, NO_3^-, NH_4^+, Na^+, K^+, Ca^{2+} and Mg^{2+}) and pH. Concentration of bicarbonate ion was also computed by a theoretical method. Ammonium, calcium and sulphate were found to have the highest concentrations in rainwater. Volume weighted mean of H^+ showed that on an average pH was in alkaline range (6.32 ± 0.16) and varied from 6.1 to 6.8. Equivalent concentration of components followed the order: $NH_4^+ > Ca^{2+} > SO_4^{2-} > HCO_3^- > NO_3^- > Cl^- > Na^+ > Mg^{2+} > K^+ > H^+$. Chemical composition of rainwater at Ballia was similar to that observed at other sites in India except with regard to the concentration of ammonium. High concentration of ammonium in rainwater in this region is due to agricultural activity, human and animal excretion. Fractional acidity was calculated and found to be very less (0.01), indicating that most of the acidity (99%) was neutralized by alkaline components.

Keywords: Rainwater, Ion concentration, pH value, Precipitation
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1 Introduction

Chemical composition of precipitation is influenced by the contents of the atmosphere through which it falls. Precipitation is an efficient pathway for removing the gases and particles from the atmosphere. In the removal process of the precipitation, gases incorporated into them are the oxides of sulphur and nitrogen, which are chemically converted into sulphuric and nitric acids[1,2]. These acids are responsible for occurrence of acid rain.

Acidic deposition in Europe and North America has shown harmful environmental effects[3-6] like acidification of soils, lakes, groundwater, etc. Population growth, agricultural activity and industrial development could lead to occurrence of this problem in the developing countries like India and China. Most of the research on precipitation chemistry[7-9] in India is focused on the large cities like Bombay, New Delhi, Calcutta, etc. Only a few studies of rainwater in rural areas[10,11] have been undertaken so far. It is often stated that precipitation over India is alkaline in nature. However, it requires more studies from rural regions to understand how long the alkaline components can fight against acidifying components over the Indian subcontinent. So, the study of acidifying species as well as neutralizing components is of equal importance in the rural environment in this region.

The quality of rainwater varies from place to place and from season to season due to variation in the rainwater composition, which is highly dependent upon the location of sampling site, topography, climate, sources of natural and anthropogenic pollutants, etc. Therefore, the study of chemical composition of rainwater at rural environments is also important to understand the effect of natural and man-made sources on the precipitation, and also, to study the possibility of long-range transport of pollutants. Considering the above, the present study is carried out at a rural environment (Ballia) in the eastern Uttar Pradesh, India during monsoon season of 2001. This is the first study of the chemical composition of rainwater in eastern Uttar Pradesh.

2 Experimental details

2.1 Sampling site

The sampling site, Ballia (25°44′N; 84°11′E; 218 m. asl.) is a small town that lies in the extreme eastern part of Uttar Pradesh, India. It is 120 km north-east

from Varanasi. In general, the climate of Ballia is moderate with average annual rainfall exceeding 100 cm. The month of August receives the heaviest rainfall in this region. The rivers Ganga and Ghaghara frequently flood the land. So the land is very fertile and a large area is under cultivation. Samples of rainwater were collected on the roof of the Satish Chandra Post Graduate College, Ballia during monsoon season (July to September, 2001). The site is quite free from vehicular activity and other major pollution sources. Figure 1 shows the sampling location on the map of Ballia, Uttar-Pradesh, India.

2.2 Sampling and analysis procedure

Samples were collected using polythene funnel of 20 cm diameter, fitted onto two-liter capacity polythene bottles. The collection gadget was placed about 15 m above the ground level. The bottle as well as funnel were washed daily with distilled water during morning and evening to avoid dry deposition. Collected samples were then stored in small polythene bottles, which were cleaned by double distilled water. A very small quantity (~5 mg) of thymol was added for preventing bio-degradation of the samples. All samples were refrigerated at 4°C in the laboratory till all ionic components were analyzed. The pH was measured immediately with the help of Elico make (model L1-120) digital pH meter with reference solutions of pH 4.01 and 7.00. Concentrations of cations (Na^+, K^+, Ca^{2+} and Mg^{2+}) were analyzed using Atomic Absorption Spectrophotometer. However, concentrations of anions (Cl^-, NO_3^- & SO_4^{2-}) were determined by Ion Chromatograph (DIONEX-100) using analytical column Ion Pac-AS4A-SC 4 mm, anion micro-membrane suppressor ASRS-1, 1.8 mM
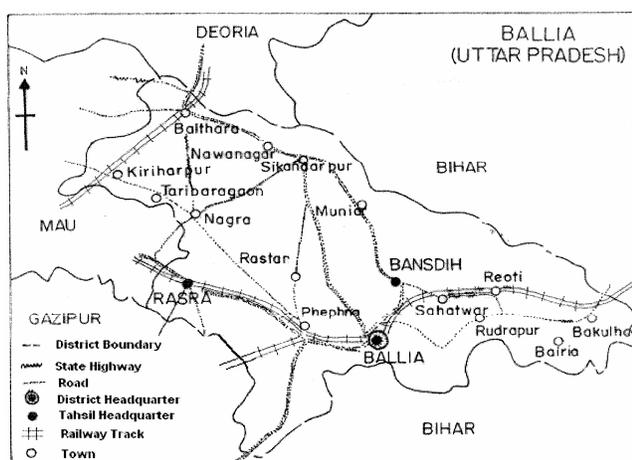

Fig. 1—Map of Ballia showing the location of sampling site (◉)

sodium carbonate/1.7 mM sodium bicarbonate as eluent and triple distilled water as regenerate. Concentration of NH_4^+ was measured by Berthelate Color-reaction method. Concentration of HCO_3^- was estimated from a theoretical relationship as given below[11].

$$[HCO_3^-] = 10^{(pH-5.05)} \ \mu eq/l$$

2.3. Data screening

Samples contaminated with dust, insects or bird droppings, etc. were removed. The data quality check was made by a statistical data reduction technique, according to which the data points outside the data range of m ± 3σ were excluded. Secondly, the quality of the data was checked by Ion Balance Technique, which also indicates the possible missing chemical ions. Linear correlation between sum of total anions and sum of total cations has been calculated. A strong correlation (0.90) was obtained between them. It means that most of the cations and anions present in the samples were measured. As the soil in this region is calcareous, there must be presence of HCO_3^- in the precipitation caused by the suspension of the soil dust. Hence, a good match between sum of cations and the sum of anions can exist only when HCO_3^- is estimated and included in the sum of anions. Less than unity, for the ratio of sum of anions to sum of cations, is also suggestive of some errors associated with measuring techniques or due to unmeasured weak organic acids. These acids are very unstable and disappear very soon.

3 Results and discussions

3.1 Ionic composition of rainwater

Average volume weighted mean (VWM) concentration (μeq/l) of various chemical constituents of rainwater collected during monsoon season of 2001 along with their pH values are given in Table 1. Also, minimum and maximum values, and standard deviation of measured ions are included in the table. It may be seen from Table 1 that ammonium, calcium and sulphate are dominant ions in Ballia rainwater. The role of these ions is more important to decide the acidity or alkalinity of the precipitation. The general trend of the abundances of different chemical constituent is as follows:

$NH_4^+ > Ca^{2+} > SO_4^{2-} > HCO_3^- > NO_3^- > Cl^- > Na^+ > Mg^{2+} > K^+ > H^+$

Table 1—Average volume weighted mean (VWM), minimum and maximum concentrations (µeq/l) along with standard deviation of various chemical species in rainwater at Ballia

	Concentration of chemical species, µeq/l										
	Cl^-	SO_4^{2-}	NO_3^-	NH_4^+	Na^+	K^+	Ca^{2+}	Mg^{2+}	HCO_3^-	H^+	pH
Average	8.9	33.0	14.8	58.4	6.5	3.6	41.1	5.2	19.7	0.5	6.3
Min.	0.6	5.2	3.9	0.5	0.4	0.3	8.0	1.7	11.2	0.2	6.1
Max.	38.2	78.4	60.2	122.0	31.3	8.7	95.5	13.2	56.2	0.8	6.8
Std. Dev.	10.4	24.3	12.6	27.7	7.7	2.9	28.8	3.4	9.1	0.2	0.2
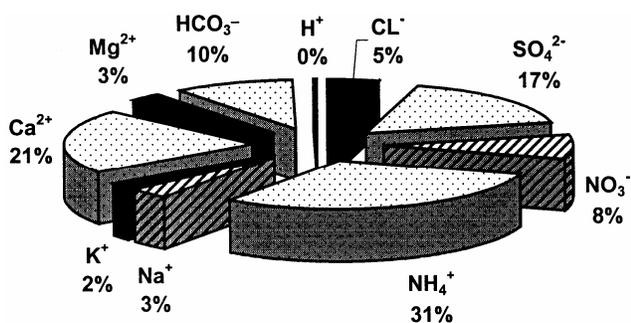
Fig. 2—Percentage contribution of each ion to total ionic mass

Table 2—Equivalent concentration ratios of ionic components w.r.t. sodium

	Concentration ratio				
	Cl^+/Na^+	Mg^{2+}/Na^+	K^+/Na^+	Ca^{2+}/Na^+	SO_4^{2-}/Na^+
Rainwater	1.37	0.80	0.55	6.35	5.09
Seawater	1.160	0.227	0.022	0.044	0.125
EF*	1.18	3.54	25.38	144.67	40.75
SSF**	89%	18%	4%	1%	2%
NSSF***	11%	72%	96%	99%	98%

* Enrichment Factor, ** Sea Salt Fraction & *** Non Sea Salt Fraction

Volume weighted average value of *p*H in rainwater was 6.32 and varied from 6.1 to 6.8, indicating that rainwater samples were alkaline in nature. This could be due to the influence of soil dust particles, which are suspended in atmosphere in coarse mode. These particles are rich in calcium compounds. Figure 2 describes the percentage contribution of each ionic constituent to the total ionic mass. The contribution of calcium is 21% of the total ionic content, while ammonium shows maximum contribution (31%) of the total ionic mass. Maximum contribution of NH_4^+ may be due to agricultural activity in this area involving action of soil-bacteria on the nitrogen compounds in the vast agricultural field surrounding the sampling site and also due to human and animal excretions in its immediate vicinity. Both calcium and ammonium ions act to balance the SO_4^{2-} and NO_3^-, which are present in rainwater. The contribution of sulphate, the acidifying component, was 17% to the total ionic mass. The contribution of nitrate was accounted as very low (8%) to the total ionic mass. Thus, acidifying potential of sulphate was higher than nitrate. These results are similar to that reported at other Indian sites (except contribution of NH_4^+)[11-13]. Contribution of NH_4^+ is half of the total cation mass and acts as a major neutralizing agent as stated above. Contributions of Na^+, Mg^{2+}, and K^+ were very low to the total ionic content.

3.2 Marine contribution

Equivalent ratios for different ionic components like Cl^-, Mg^{2+}, K^+, Ca^{2+} and SO_4^{2-} were calculated with respect to sodium by considering sodium completely from marine origin and are shown in Table 2. Ratios of major sea salt components are found to be constant in the seawater[14]. Comparison among them reveals that all the ratio values in rainwater are found to be higher than that of seawater values except sea-salt. It indicates the dominance of non-marine contribution to above components, especially influence of crustal sources. The ratio value of Cl^-/Na^+ was found to be near to the seawater. Also, strong correlation was observed between Cl^- and Na^+, which indicates influx of marine spray from the Bay of Bengal during southwest monsoon period and from soil dust in this region. Similar results were obtained when sea-salt fraction (SSF) and non-sea-salt fraction (NSSF) were calculated by considering sodium as the reference element from marine origin, which are also shown in Table 2 using the relation:

$$NSSF = \{[X]-[Na^+] \times r\}/[Na^+]$$

where, [X] is concentration of component X, $[Na^+]$ the concentration of Na^+ and *r* the ratio of X to Na^+ in seawater. The values of NSSF for Cl^- (11%), Mg^{2+} (72%), K^+ (96%), Ca^{2+} (99%), and SO_4^{2-} (98%) indicated presence of non-marine source in Ballia

rainwater for Ca^{2+}, K^+ and SO_4^{2-}. Enrichment factor (EF) for above five species with respect to sodium was also estimated by the following equation:

$$EF = [X/Na^+]_{rainwater}/[X/Na^+]_{seawater}$$

The enrichment factors are also shown in Table 2. It shows that all components are enriched except sea salt. This result also confirmed the influence of local sources other than marine.

3.3 Event wise distribution of ionic elements

Since the chemistry of rainwater is greatly influenced by the ionic species mainly NH_4^+, Ca^{2+}, SO_4^{2-}, etc., so it is important to discuss variations of these species. Figure 3 shows the event wise variations of ionic elements. From the figure, it is revealed that some of the ions show very close relationship with each other, e.g. Na^+ and Cl^-. NH_4^+ also shows close relation with NO_3^- and Cl^-. Ca^{2+} and SO_4^{2-} follow somewhat similar trend. These results
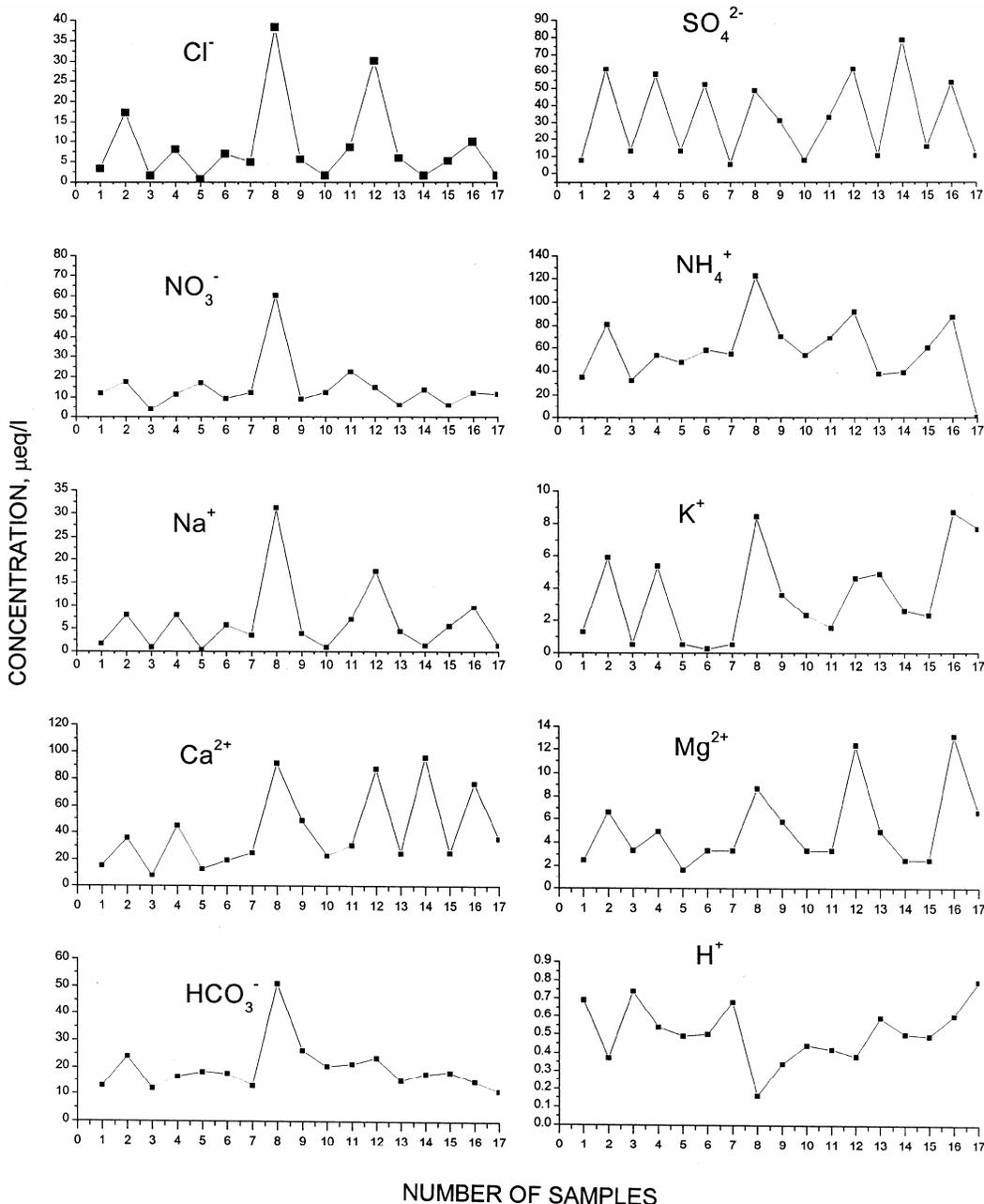

Fig. 3—Event-wise distribution of ionic elements

indicate possibility of these ions in the salt form like NaCl, NH_4NO_3 and $CaSO_4$. Crustal ions (Ca^{2+}, Mg^{2+} and K^+) show by and large a similar trend. There is inverse relationship of H^+ ion with NO_3^- HCO_3^- and NH_4^+.

3.4 Determination of chemical sources

Sources of measured parameters in rainwater were examined through the analysis of linear correlation. The correlation matrix for all samples is given in Table 3. We considered the correlation as good if $r >$ 0.6 and marginal if $0.47 < r < 0.6$ at 95% confidence level. The sulphate showed good correlation with Ca^{2+} ($r = 0.75$) and marginal with NH_4^+ ($r = 0.50$) indicating that it is in the form of $CaSO_4$ and $(NH_4)_2SO_4$ as important compounds in precipitation. Sulphate show poor correlation with pH, which means complete neutralization. In this study, it was seen that there is strong correlation between Na^+ and Cl^- ($r = 0.96$). Also, sodium showed good correlation with Mg^{2+} ($r = 0.63$). This indicates that some part of magnesium is also brought from marine sources. Chloride showed good correlation with NO_3^- ($r = 0.75$), Mg^{2+} ($r = 0.66$), Ca^{2+} ($r = 0.63$) and K^+ ($r = 0.53$), which may be due to soil blown dust from old salt deposits. Ca^{2+} also showed quite good correlation with Mg^{2+} ($r = 0.66$), Na^+ ($r = 0.64$), K^+ (0.61) and Cl^- ($r = 0.63$). Also, Na^+, K^+, Ca^{2+} and Mg^{2+} have high correlation coefficients between one another, implying that they might have originated from the same source, the soil. NO_3^- was significantly correlated with Na^+ ($r = 0.82$) and Ca^{2+} ($r = 0.49$). It means that nitrate is also in the non-acidic salt form. The source of ammonium is different from the soil and sea. It is common for ammonium to be correlated with sulphate and nitrate in the form of NH_4NO_3 over $(NH_4)_2SO_4$. In the present study, however, it showed better correlation with NO_3^- ($r = 0.65$) than SO_4^{2-} ($r = 0.50$).

3.5 Neutralization

The ions NH_4^+, Ca^{2+}, Mg^{2+} and K^+ are considered as the neutralizing agents. The contribution of each of them and their importance can be visualized by computing neutralization factors for each of them[15]. To estimate the concentrations of non-sea-salt fraction for SO_4^{2-}, Ca^{2+}, Mg^{2+} and K^+ in rainwater, sodium was assumed to be reference element and the equations used was as given below:

$$[nss\text{-}SO_4^{2-}] = [SO_4^{2-}] - 0.125 \times [Na^+]$$

where, $[nss\text{-}SO_4^{2-}]$, $[SO_4^{2-}]$, and $[Na^+]$ denotes the concentrations in µeq/l. The coefficient 0.125 for $[nss\text{-}SO_4^{2-}]$ was taken from the ratio for its concentration with respect to sodium in seawater. Neutralization factors for above four components were calculated. The order of neutralization along with NF values was found as:

$$NF\ [NH_4^+]\ (1.243) > NF\ [Ca^{2+}]\ (0.870) > NF\ [Mg^{2+}]\ (0.080) > NF\ [K^+]\ (0.073)$$

This result also confirmed that the major neutralization occurred due to the contribution of ammonia. Presence of higher values of ammonia is mainly due to the agricultural activity along with human and animal excretion around the sampling site. Calcium also gives significant contribution to the neutralization process. Calcium mainly occurred in the precipitation from soil erosion. The major role for neutralizing component in precipitation in Indian regions is calcium, which is contributed by soil dust in ambient air[12,16,17].

3.6 Potential index

Two types of index can be used for evaluating the qualitative characteristics of ions in rainwater. Fujita[18] defined the value of sum of $[nss\text{-}SO_4^{2-} + NO_3^-]$ as the

Table 3—Correlation matrix of ionic components

	Cl^-	SO_4^{2-}	NO_3^-	NH_4^+	Na^+	K^+	Ca^{2+}	Mg^{2+}	pH
Cl^-	1.00								
SO_4^{2-}	0.48*	1.00							
NO_3^-	0.75**	0.26	1.00						
NH_4^+	0.83**	0.50*	0.65**	1.00					
Na^+	0.96**	0.45	0.82**	0.83**	1.00				
K^+	0.53*	0.37	0.42	0.36	0.57*	1.00			
Ca^{2+}	0.63**	0.75**	0.49*	0.55*	0.64**	0.61**	1.00		
Mg^{2+}	0.66**	0.45	0.28	0.56*	0.63**	0.78**	0.66**	1.00	
pH	0.77**	0.42	0.80**	0.83**	0.79**	0.42	0.52*	0.29	1.00

*Signif. LE 0.05 ; **Signif. LE 0.01(2-tailed)

acidifying potential index (AP), and [nss-Ca^{2+}+NH_4^+] as the neutralizing potential index (NP). Since volcanic emission of sulphur contributes little in the total emission of sulphur over Indian region, so acidifying potential index can be used to explain the effects of anthropogenic activities. Also, there are lots of broad production sources of calcium (e.g. production and combustion processes, cement factories, dust storms, etc.) and ammonia (e.g., agricultural activity and excretion) over Indian continent so that the concentration of nss-Ca^{2+} and NH_4^+ can be used as an index of neutralization.

Rainwater analysis at Ballia during monsoon season showed value of [AP] as 47 (µeq/l) and value of [NP] as 99 (µeq/l). The relationship [NP > AP] indicates that although the value of [AP] is high but value of NP was much higher. The ratio of [NP/AP] gives clear picture of acidity/alkalinity. The value of this ratio comes out to be approximately double. This means that the neutralizing potential is approximately more than double the acidifying value. Ammonium and calcium containing particles are sufficient to neutralize the acidity, which has occurred due to anthropogenic (man-made and long-range transport) sources.

3.7 Fractional acidity

Fractional acidity was measured, which is the acidity generated by the strong acidic components and is not neutralized at all. It is given by the following formula[19].

Fractional acidity= $[H^+]/\{[SO_4^{2-}] + [NO_3^-]\}$

In our study, Fractional acidity (FA) was found to be 0.01. It means alkaline constituents neutralized about 99% of acidity. Relative contribution of NO_3^- to the acidification can be figured out by calculating the following ratio:

Contribution of NO_3^- to the acidification = $[NO_3^-]/\{[NO_3^-] + [nss-SO_4^{2-}]\}$

Above equation shows that 31% of acidity in the rain is due to the NO_3^-. As SO_4^{2-} is the other major contributor to the acidity, it can be said that the remaining 69% of acidity may be due to SO_4^{2-}. If cations were not available in the lower troposphere, the atmosphere in this region would have been acidic in nature.

4 Comparison with other studies

As there are no point sources of pollution at the site, being located away from the urban areas, it is summarized that the observed concentrations of the various ionic species may reflect regional background values. Hence, the measured concentrations in rainwater at Ballia have been compared with available data from Kalyan (industrial coastal station in the north-east of Mumbai), Gopalpura (rural station in Agra region, 52 km south-west) and Sinhagad (a hill station on a mountaintop in the Western Ghats near Pune) and are shown in Table 4. Kalyan is one of the highly industrialized locations in the metropolitan city of Mumbai. It was seen from the table that the value of pH at Ballia is equal to those at Gopalpura and Sinhagad.

It is evident from Table 4 that the concentration of ammonium in rainwater at Ballia is about 4, 1.5 and 9 times higher than the concentration reported in rainwater from Kalyan, Gopalpura and Sinhagad, respectively. The reason for high concentration of ammonium is already discussed in Section 3.1. Concentration of nitrate at Ballia is more than double of that at Sinhagad. However, it is four and three times lower as compared to that at Kalyan and Gopalpura, respectively. Concentration of sulphate at Balhia is equal to that at Sinhagad but three times lower than that at Kalyan. Concentration of sodium and chloride are eight and three times lower than those at Sinhagad and Gopalpura, respectively. However, they are one-and-a-half order of magnitude lower than those at Kalyan, which is a coastal station. Concentration of calcium is lower at Ballia than all

Table 4—Chemical composition of rainwater at different sites in India

| | Concentration of chemical species, µeq/l | | | | | | | |
	pH	Ca^{2+}	Mg^{2+}	K^+	Na^+	NH_4^+	NO_3^-	Cl^-	SO_4^{2-}
Ballia	6.3	41	5	4	7	58	15	9	33
Kalyan[20]	5.3	130	48	6	147	14	66	134	110
Gopalpura[10]	6.5	134	78	3	19	43	43	31	15
Sinhagad[21]	6.4	77	19	3	59	6	6	73	30

other stations, because alkaline aerosols settled down on the earth with the commencement of rains.

5 Conclusions

Chemical composition of rainwater in a rural environment of Ballia, eastern Uttar Pradesh has brought out the following salient features: NH_4^+, Ca^{2+} and SO_4^{2-} are the three dominant ions found in rainwater samples. Role of these ions are important for deciding acidity or alkalinity of rainwater. The average (VWM) *p*H value was found to be 6.32, which shows alkaline nature of rainwater. Significant contribution of NH_4^+ is due to the agricultural activity, human and animal excretion. Correlation analysis reveals that sodium, chloride and some part of magnesium are brought from marine sources during monsoon period. Most of the SO_4^{2-} was found to be associated with Ca^{2+} and Mg^{2+} in the form of $CaSO_4$ and $MgSO_4$. Some part of SO_4^{2-} was also associated with NH_4^+ and in the form of $(NH_4)_2SO_4$. NO_3^- was also found to be in the form of nitrate salts formed with crustal compounds like Ca^{2+} and K^+. Also, it shows good correlation with ammonium in the form of NH_4NO_3. Existence of compounds of ammonium nitrate dominates over compounds of ammonium with sulphate. Equivalent ratio values of major ionic components are found to be higher than that of seawater values except sea salt, giving indication of dominance of non-marine contribution. Neutralization factors for NH_4^+ and Ca^{2+} are found to be higher, which indicates that major neutralization occurred due to the contribution of ammonium and calcium. The relationship between NP and AP [NP > AP] holds good for our study. Fractional acidity was found to be 0.01, which means that most of the acidity (about 99%) was neutralized. Ammonium and calcium ions are sufficient to neutralize the acidity occurring due to man-made sources and long-range transport sources.

Acknowledgement

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