Chemical characterization of rainwater at Akkalkuwa, India

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ABSTRACT. The chemical composition of rainwater changes from place to place and region to region under the influence of several major factors, viz., topography, its distance from sea and overall rainfall pattern. The present study investigated the chemical composition of precipitation at Akkalkuwa, district Nandurbar, in the State Maharashtra during southwest monsoon. The rainwater samples were collected on event basis during June-September 2008 and were analyzed for pH, major anions (F, Cl, NO₃, SO₄) and cations (Ca, Mg, Na, K, NH₄). The pH varied from 6.0 and 6.8 with an average of 6.29 ± 0.23 indicating alkaline nature and dominance of Ca in precipitation. The relative magnitude of major ions in precipitation follows the pattern as Ca>Cl>Na>SO₄>NO₃>HCO₃>Mg>K>F. The Neutralization factor (NF) was found to be NF Ca = 0.95, NF NH₄ = 0.31, NF Mg = 0.27 and NF K = 0.08 indicating below cloud process in which crustal components are responsible for neutralization of anions. Significant correlation of NH₄ with SO₄ and NO₃ was observed with correlation coefficient of r = 0.79 and 0.75, respectively.

Key words – Acid-Neutralization potential, Major ions composition.

1. Introduction

The rainwater chemistry of monsoon is a result of complex hydrological processes. Precipitation is the main process which acts upon removal of atmospheric particles originated either from anthropogenic or natural sources. Investigation of chemical composition of rainwater provides an understanding of prevailing state of the atmospheric environment, source types that contribute and enhance understanding of local, regional, national and global dispersion of pollutants and their hydrological processes. The chemical composition of rainfall also reflects the quality of the air through which it falls and hence it forms a useful indicator in precipitation chemistry. Furthermore, the chemicals carried by the rain can affect ecosystems, sometimes positively but usually negatively (Hideaki et al., 2008). Rainfall is one of the most effective ways of removing atmospheric pollutants. In a study of rainfall contribution to constituent loads in urban areas, researchers have generally found composition of the rainwater data set is predominantly influenced by three factors namely soil dust, sea spray and anthropogenic (Spanos et al., 2002). Many a times, studies have generally reported the alkaline nature of rainwater, possibly due to the contribution of soil-derived particles in the atmosphere, which are found to buffer its acidity, during a below cloud scavenging process (Budhawant et al., 2009).

The village Akkalkuwa is untouched by urbanization, dominated by adivasis tribes and having less vehicular activities in the area. The study was undertaken to describe the quality of rainwater in pristine environment as the location is flanked by seven hills of
Satpuda range. The present investigation is the first effort to collect rainwater samples in a pristine tropical rural site of India and to determine the chemical composition of rainwater on a set of quality-checked data, identify the potential natural and anthropogenic sources of the different chemical content of precipitation contributing to rainwater chemistry.

2. Methodology

Akkalkuwa lies in Satpuda range of hills, with Narmada forming northern boundary. Sampling site lies at village-Akkalkuwa, district Nandurbar, Maharashtra represents a typical rural atmosphere of a semi-arid region in north western side of Maharashtra State (Fig. 1). The southern and western boundaries are occupied by Gujarat. This area is hilly terrain with more than fifty percent area falling under forest. The Akkalkuwa taluka occupies an area of 846 km². The area is covered in Survey of India topographical maps as 46G/13, 46G/14 46K/1 and 46K/2. The area is situated between various parallel ranges of Satpudas, which are an extension of the spurs of Sahyadris and lie in continuation with the trends of Vindhyas. Agriculture is the main occupation and no industries are present within 10 km area. The soils are deep black to shallow black brown and alluvial soils of southern regions. The population density of the area is about 115-150 persons km² (Mahajan & Kale 2006). As per the classification of forest types of India, the vegetation in the region can be classified under subgroup 3B/C2 of group 3 and interpreted as Southern Moist Tropical Mixed Deciduous Forests. The major land use pattern in the district comprises of 6264, 2798, 940 sq km as agriculture, forest cover and wasteland respectively. The climate of the region is generally hot and dry. Summer is from March to mid of June. Summer season is usually hot and dry. During the month of May the summer is at its peak. Temperatures can be as high as 45 °C during the peak of Summer. The Monsoon sets in during the mid or end of June. During this season the weather is usually humid and hot. The northern and western regions receive more rainfall than the rest of the region. The average rainfall is 859 mm through the district.

Rainwater samples have been collected at Jawahar Navodaya Vidyalaya (JNV), during the monsoon season of year 2008, using a polythene funnel of 20 cm diameter fitted in 2 litre capacity polythene bottle at the roof top of residential colony premises. The collector has been placed on the terrace of first floor at 1.5 m above the roof which is 20-25 feet above the ground level. The bottle as well as the funnel has been cleaned using triple-distilled water to avoid any dry deposition of gaseous and particulate species. Collected samples have been stored in small polythene bottles also cleaned by triple-distilled water. Thymol (5 mg) was added to these samples for preventing any biological degradation. A total of 34 samples have been collected during July-September 2008. The samples were immediately measured for pH with digital pH meter (calibrated with reference to pH 4.01 and 7.0) in the laboratory within the campus. All samples were refrigerated at 4 °C in the laboratory till the analysis was over.

The samples were analyzed for cations and anions by ion chromatography (ICS 3000). The limits of detection for cations and anions were 1 ppb in Dionex ion chromatograph. The analytical precision was maintained through running of known standards (Salve et al., 2006, and 2008). HCO₃ exists in precipitation through dissolution of atmospheric CO₂ and other particulate carbonate species. Concentration of HCO₃ is being significant at the alkaline pH values encountered in most of the rain samples. As HCO₃ is seldom determined experimentally in the present study, it was calculated using theoretical relation between pH and HCO₃.

Samples contaminated by bird’s droppings and dead leaves were discarded. The remaining samples were subjected to the quality check on the basis of ionic balance by estimating the ratio value of the sum of anions to the sum of cations. A strong correlation coefficient of 0.86 between sum of anions and sum of cations indicated that most of the ions were analyzed and quantified. However, less than unity ratio points out that some of the anions
TABLE 1
Summary of major ions in rainwater

| Major ions | Min   | Max   | Average | SD   | Skewness | Kurtosis | %     |
|------------|-------|-------|---------|------|----------|----------|-------|
| pH         | 6.01  | 6.81  | 6.29    | 0.23 | 0.90     | -0.01    | -     |
| F          | 1.10  | 3.47  | 2.02    | 0.63 | 0.63     | 0.22     | 1.21  |
| Cl         | 26.42 | 35.66 | 31.54   | 2.72 | -0.29    | -1.02    | 18.99 |
| SO₄        | 17.69 | 26.36 | 22.41   | 1.86 | -0.60    | 0.74     | 13.49 |
| NO₃        | 12.13 | 17.04 | 14.52   | 0.92 | 0.13     | 1.86     | 8.74  |
| HCO₃       | 5.26  | 34.00 | 11.85   | 7.75 | 1.71     | 2.19     | 7.13  |
| Na         | 19.22 | 26.24 | 23.21   | 1.80 | -0.28    | -0.79    | 13.97 |
| Ca         | 27.38 | 41.03 | 35.35   | 2.70 | -0.53    | 1.19     | 21.28 |
| K          | 1.72  | 5.12  | 3.06    | 0.90 | 0.25     | -1.00    | 1.84  |
| Mg         | 7.89  | 13.24 | 10.06   | 1.43 | 0.72     | -0.08    | 6.06  |
| NH₄        | 9.24  | 15.42 | 11.55   | 1.22 | 0.62     | 1.54     | 6.95  |
| H          | 0.15  | 0.97  | 0.57    | 0.24 | -0.09    | -1.00    | 0.34  |

All values of major ions in μeq/l except pH.

Ion balance is an important parameter for data quality assessment. Data quality of each precipitation events was checked by ionic balance. The data was rejected in the event of non-conformity of quality criteria, which allowed for 15% deviation of ion balance ratio (sum of cations/sum of anions). Based on the principle of electro-neutrality, the quality of chemical analysis, could be assessed by the ionic balance considering all the major ions in a single sample. The per cent error (E%) was calculated by using equation reported elsewhere (Singh et al., 2007) and the error was obtained as 2.02% which was found to be within ± 5%.

3. Results and discussions

3.1. Skewness and Kurtosis

The skewness and kurtosis statistics provides information about the central tendency and variability of major ions. The skewness analysis indicates the distribution shape and variation of major ions based on the mean and the median values. If the mean is less than the median, the distribution is skewed to the left and few points with low values disproportionately affect the mean; and vice versa. The kurtosis parameter characterizes the relative peak-holding or flatness of a distribution compared with the normal distribution. Positive kurtosis implies a relatively peaky distribution; however, negative kurtosis corresponds to a relatively flat curve (Mouli et al., 2005). It was noticed from the analysis data that the skewness was positive for pH, F, NO₃, HCO₃, K, Mg and NH₄ indicating that the distribution has a long tail extending to the right and negative for Cl, SO₄, Na, Ca and H; while the kurtosis values were negative for pH, Cl, Na, K, Mg and H and positive for remaining ionic species (Table 1).

3.2. Variation in pH

The precipitation chemistry mainly deals with the air pollutant loading in the atmosphere which falls with rainwater on the ground. The loading depends on the concentrations in rainwater and the rainfall amount. The pH of precipitation ranged between 6.0 and 6.8 with an average value of 6.29 ± 0.23 (Table 1). The distribution of pH of the precipitation samples collected during monsoon indicated that all the precipitation samples had pH in the basic range as compared to the reference value of 5.6 for cloud water. These values are higher than 5.6 for unpolluted rain (Charlson & Rhode, 1982). The relatively higher pH measured in this study was due to neutralization of acidity in precipitation by CaCO₃. The acidity in precipitation depends on the concentration of acid-
TABLE 2
Enrichment factor (EF), sea salt (ss) and non sea salt (nss) fractions of major ions in rainwater

| Major ions | Cl/Na | K/Na | Mg/Na | Ca/Na | SO4/Na | NO3/Na |
|------------|-------|------|-------|-------|--------|--------|
| Sea water  | 1.16  | 0.037| 0.038 | 0.12  | 0.25   | 0.00002|
| Rainwater  | 1.35  | 0.134| 0.435 | 1.526 | 0.966  | 0.62   |
| SS (%)     | 85.33 | 27.69| 8.73  | 7.86  | 25.88  | 0.0027 |
| NSS (%)    | 14.67 | 72.31| 91.27 | 92.14 | 74.12  | 99.99  |
| EF         | 1.17  | 3.6  | 11.45 | 12.71 | 3.86   | -      |

3.3. Major ions constituents in precipitation

Atmospheric deposition processes are inherently variable causing considerable variation in precipitation composition at local and regional level. Typical wind blown dust in tropical regions might have its impact on the results. The summary of volume weighted mean (vwm) concentration of major ions, together with pH in precipitation is presented in Table 1. The average and standard deviation of major ions was found to be 166 ± 10 µeql⁻¹. The major ions play a significant role in deciding the acidity or alkalinity in precipitation. The relative magnitude of major ions in precipitation followed the pattern Ca>Cl>Na>SO₄>NO₃>HCO₃>NH₄>Mg>K>F>H. The relative percentage contribution of total anions and cations was calculated from the average composition and are depicted in Fig. 2. The total anions and cations contributed 49.56% and 50.43%, respectively indicating that most of the major ions were measured. In attempting to achieve ion balance with the major ions, the deficit is largely found to lie with anions. Some escaped ions like organic acid, acetate, formate etc. were not measured and not accounted in the study. The charge balance between cations and anions suggests that the organic acids had a negligible effect on the rainwater composition (Saxena et al., 1996).

3.4. Sea salt and non sea salt contributions

The precipitation occurred during monsoon is due to the southwest monsoon originating from the Bay of Bengal and the Arabian Sea, the precipitation contribution may reflect its marine origin. Sea salt ratios in precipitation samples were calculated using Na as the reference element assuming all Na to be of marine origin. All ratios were found to be higher at this site than recommended seawater ratios (Table 2). These evaluated values may be due to the influence of local terrestrial/soil sources. The observed precipitation ratio of Cl/Na (1.35) was higher than seawater ratio (1.16) indicating influence of long range transport of constituent in precipitation. The non sea salt (nss) contributions of ionic constituent, viz. nss-Ca was found to be 92% suggesting their crustal origin whereas nss-Mg, nss-K and nss-SO₄ showed its contribution as 91, 72.3 and 74.1% indicating influence of soil sources.

3.5. Neutralization factors

Calcium and ammonium are known as the principal neutralizing agents of the acidity. The main source of calcium is the soil with high CaCO₃ content and the
source of ammonium is the ammonium based fertilizers (site surrounded by agricultural field). The role of NH₄, Mg, K and Ca has been validated by calculating neutralization factors reported elsewhere (Kulshrestha et al., 2003). The factors estimated for the present study were 0.95 for Ca, 0.31 for NH₄, 0.27 for Mg, and 0.08 for K (Table 3), indicating that Ca and ammonium were dominant species in neutralization followed by Mg and K in precipitation. The coarse-mode Ca aerosols seem to be a major component for neutralization of rainwater acidity at most of the Indian sites. Therefore dominance of calcium was attributed to soil dust in ambient air whereas ammonium sources attributed to bacterial decomposition of urea in animal excreta and emissions from natural or fertilized agricultural soils in rural environment and also contribution from gaseous NH₃ and particles containing NH₄ in clouds and precipitation (Khare et al., 2004).

### 3.6. Acid-neutralization potential of major ions

To assess the balance between acidity and alkalinity, ratio of NP/AP was computed as, NP/AP = nss-Ca + [NH₄] / [nss-SO₄] + [NO₃]. The acidic and neutralization potential values were estimated to be 36.9 and 43.2 μeq/l respectively. The ratio [NP>AP] gives the clear picture of acidity or alkalinity. The average value was 1.17, indicating dominance of alkaline constituents in preventing acidification of rain water (Safai et al., 2004). Acidity of precipitation is controlled mainly by the strong acids, e.g., H₂SO₄ and HNO₃. Considering both SO₄ and NO₃ as the main acidifying components of rain, Fractional Acidity (FA) was computed using following equation FA = (H⁺) / [(nssSO₄) + (NO₃)]. If this ratio is one, it is considered that the acidity generated by these strong acids is not neutralized at all.
TABLE 5
Principal component analysis (PCA) of major ions in rainwater

| Major ions | PCA1 | PCA2 | PCA3 | Communalities |
|-----------|------|------|------|---------------|
| Ca        | 0.83 | 0.05 | 0.197| 0.734         |
| Cl        | 0.08 | 0.10 | 0.942| 0.898         |
| F         | 0.08 | 0.82 | 0.170| 0.711         |
| H         | -0.01| 0.875| -0.175| 0.797       |
| HCO$_3$   | -2.75| -0.824| 0.136| 0.797         |
| K         | 0.08 | 0.802| 0.177| 0.682         |
| Mg        | 0.303| -0.697| 0.410| 0.745         |
| Na        | 0.083| -0.138| 0.928| 0.819         |
| NH$_4$    | 0.898| -0.080| 0.073| 0.819         |
| NO$_3$    | 0.902| 0.054| -0.111| 0.829       |
| SO$_4$    | 0.935| 0.218| 0.057| 0.925         |
| % of variance | 33.8 | 29.1 | 16.9 |               |
| Eigens value | 3.72 | 3.21 | 1.86 |               |

The average FA value was 0.018, indicating that about 99% acidity was neutralized by alkaline constituents. Relative contribution of NO$_3$ to the acidification was computed using a ratio $(\text{NO}_3) / [(\text{NO}_3) + (\text{nss-SO}_4)]$ and its average value was 0.46, showing that about 46% of acidity of rain was due to NO$_3$ and 54% due to SO$_4$.

3.7. Correlation matrix of major ions

Correlation matrix is a common way of hypothesizing potential precursors of ions in rainwater samples. Correlation between ions suggests the likely sources of pollutants and also indicates the gaseous reaction occurring in the atmosphere (Kumar et al., 2002). In the present study, NO$_3$ and SO$_4$ show good correlation ($r = 0.80$) in rain samples indicating their origin from similar sources (Table 4). It is possible that a fraction of NO$_3$ and SO$_4$ may be derived from soil as a primary pollutant or may be associated with Ca, Mg and Na after the neutralization process. This is corroborated by significant correlation between Ca and SO$_4$ ($r = 0.78$), Ca and NO$_3$ ($r = 0.65$) respectively. Na and Cl which are essential components had good correlation with each other ($r = 0.87$) implying a common origin. Significant correlation of NH$_4$ with SO$_4$ and NO$_3$ was observed as $r = 0.79$ and 0.75 respectively. In the atmosphere ammonia generally occurs as NH$_4$(SO$_4$)$_2$ (Seinfeld, 1986), but it appears that NH$_4$ is largely associated with SO$_4$ followed by NO$_3$. NH$_4$(SO$_4$)$_2$ and NH$_4$NO$_3$ is possibly formed by the reaction of H$_2$SO$_4$ or HNO$_3$ with NH$_3$ on moist soil surfaces (Satsangi et al., 1998).

3.8. Principal component analysis (PCA)

To explore the correlations among observed variables and potential major sources of chemical species in precipitation, PCA was carried out for three major factors from the 34 data set of rainwater samples (Table 5). The three factors together explain 80% of the total variations caused by all variables. PAC1 explained 33.8% of variance due high loading of Ca, NO$_3$, SO$_4$ and NH$_4$ which clearly reflected their origin from soil sources. Similarly soil-derived Ca with NO$_3$ and SO$_4$ suggested that they are directly released from soil and contribute to neutralization reaction in atmosphere, prior to precipitation. The presence of NH$_4$ is linked to the co-occurrence of NH$_4$ with NO$_3$ and SO$_4$ in precipitation, which may be caused by dissolution of aerosols/secondary pollutants in rainwater containing (NH$_4$)$_2$SO$_4$ and NH$_4$NO$_3$ or biogenic sources (NO$_3$ and NH$_4$) activities such as cow dung cakes combustion for heating and cooking and the excretion of animals. PAC2 explained 29.1% of variance with high loading of K, F and H, which indicated presence of low concentration of H in the precipitation whereas presence of K and F are attributed to wood burning and brick kiln respectively in the atmosphere of study area. The PCA3 explained 16.9% of variance with high loading of Na and Cl suggesting the
contribution of sea salt and long range transport of oceanic winds.

3.9. Geographical comparison

The chemical composition of rainwater was compared with some other selected Indian sites of rural environment (Table 6). The dominance of calcium was reported in almost all rural locations indicating contributions from soil derived material (Tiwari et al., 2006 and 2007). The Na and Cl are mostly derived from the oceanic circulation; hence contribution of sea decreases with increasing distance from the sea coast. The concentration of SO₄ and NO₃ was lower as compared to Ballia attributed to background regional sources besides vehicular traffic activities. The concentration of NH₄ was lower as compared to others indicates low dissolution in rainwater as pH was in alkaline range.

4. Conclusion

The study of chemical composition of rainwater was carried out at Akkalkuwa during the period June-September 2008 represented the first contribution in the area for understanding rainwater chemistry in rural environment. The following conclusions were drawn:

(i) The rainwater was typically alkaline as pH ranged from 6.01 to 6.8 with a median value of 6.29 ± 0.23.

(ii) Among the ions, Ca made the highest contribution indicating dissolution of soil dust into the rain samples, which reflected a major crustal influence based on the results of the rainwater ion composition.

(iii) The acidity of the rainwater was significantly neutralized by natural alkaline soil dust and ammonium ion also played a significant role in the neutralization process.

(iv) There was a strong correlation between NH₄ and NO₃ and SO₄ in precipitation which may be due to dissolution of aerosols/secondary pollutants or biogenic sources.

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