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Short Communication

Chemical characterization of Rainwater at Agra, UP, India

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Abstract

The present study reports the rainwater composition during the monsoon of 2010 at Sikandra (Agra) an industrial site. The precipitation samples were analyzed for pH, conductivity, major anions (F^-, Cl^-, SO^{2-}_4, NO^-_3) and cations (K^+, Na^+, Ca^{2+}, Mg^{2+}, NH^+_4). The pH value varied from 6.5 – 8 indicating the alkaline nature of rainwater. Ratio of total anion to total cation is below 1. The results of neutralization factor show that the major neutralizing component was Ca^{2+}. Good correlation among Ca^{2+}, Mg^{2+}, NO^-_3 and SO^{2-}_4 with one another may be due to these species which commonly occur in the soil. Good correlation of NH^+_4 with SO^{2-}_4 suggested that they are present in rainwater as $(NH_4)_2SO_4$.

Keywords: Rainwater, scavenging ratio, neutralization factor, major ions.

Introduction

Rainwater plays an important role in removal of atmospheric air pollutants from the atmosphere and impacting ecosystem as well as human artifacts[1]. This removal of particles is known as scavenging process which occurs as in-cloud and below cloud scavenging. The scavenging process affects chemical composition and pH of rainwater. The pH is an indicator of acidic and basic environment through which clouds have passed. The reference pH of rainwater is 5.6. In India, pH values are reported higher than this reference pH which varies from 6 to 7.5 in most of the studies[2-5]. The composition of rainwater helps us in understanding that which sources are contributing to the atmospheric pollutants[4]. The rainwater composition varies from site to site and regions to regions due to different sources influencing the air pollutants.

Although many studies have been carried out in Indian subcontinent on precipitation[2-4,6,7]. But there are still gaps between understanding the complete knowledge of rainwater chemical composition throughout year round. The present study will help in understanding the complete knowledge of rainwater. The objective of the present study was to determine major ions (cations and anions) present in rainwater and to determine their possible sources.

Materials and method

Sampling was carried out at Agra (27°10′N, 78°05′E, and 169 m.s.l.) which is located in the north central part of India. It is a semiarid area because two thirds of its peripheral boundaries (SE, W and NW) are bounded by the Thar Desert of Rajasthan. Meteorologically the year is divisible into three distinct seasons; summer (March–June), monsoon (July–September) and winter (October–February). The monsoon season is characterized by high relative humidity which ranges from 70 to 90%, and temperature ranges from 24 to 38°C. In Agra, there are various small scale industries like ferrous and non-ferrous metal casting, chrome and nickel plating units, electroplating industry, engineering works and chemicals. Agra is famous for Petha (famous Indian confectionary) and shoe industries which contribute to aerosol loading through their solid waste dumping and incineration.

Manual samples were collected using polyethylene bottles and funnels washed with HNO_3 and deionized water at an industrial site of Agra (Sikandra). As the rain began, the collectors were deployed and immediately withdrawn when the rain ceased. pH was measured after the sample collection and the calibration of pH meter was done before and after each measurement. After pH measurements, the remaining sample was filtered through a prewashed Whatman filter No. 41 into precleaned polyethylene bottles. Until analysis, all the samples were preserved at 4°C in a refrigerator.

The concentrations of major anions (F, Cl, NO_3 and SO_4) and major cations (Na, K, NH_4, Ca and Mg) were analyzed by Ion Chromatography using Dionex ICS 1100 Ion Chromatograph as described in Satsangi G.S.et al.[8].

Results and discussion

Ionic Composition: The average, minimum and maximum concentrations (μeq/L) of major ionic components, pH and conductivity are presented in Table-1. The concentration of major ionic species has the following order: Ca > Cl > SO_4 > K > Na > NO_3 > Mg > NH_4 > F. The abundance of crustal sources at the present site is reflected in the results. Total cations are

more abundant than total anions indicating dominance of crustal sources. Previous studies at the present site also showed similar results[9].

The pH of rainwater was alkaline as compared to the reference level, 5.6[10]. The average value of pH was found to be 6.8 ± 0.5 ranging from 6.1 to 8.5. When H^+ concentration is less than the H^+ concentration due to only carbonate ion, alkaline precipitation occurs, this is due contribution of soil oriented salts like $CaCO_3$, Na_2CO_3, sea salt etc to rain[4].

In order to determine the local or long range source of regions of various constituents present in rainwater, the percentage contribution of sea salt fraction (SSF %) and non sea salt fractions (NSSF %) have been calculated using the following equation[11]:

$SSF\ \% = 100\ Na_{rain}\ (X/Na)_{sea} / X_{rain}$

Where: X is the element of interest

$NSSF\ \% = 100 - SSF\%$

The NSSF% (non-sea salt fraction) for different ions follows the trend: Ca (94.6%) > K (93.4%) > SO_4 (92.6%) > Mg (68.4%) > Cl (65%) showing significant influence of local sources other than marine influence at this site.

Table-1: pH and average concentration levels of major ions in precipitation.

Parameter (μeq/L)	Minimum	Maximum	Average
Na	5.8	173.5	77.2
NH_4	0.93	21.4	3.3
K	7.7	511	121.3
Ca	15	758.1	263.8
Mg	5	168.3	52.4
Cl	20.9	982.1	117.2
F	0.34	1.5	0.8
NO_3	12.8	301.4	63.9
SO_4	18.1	587.2	112.2
pH	5.6	7.4	6.8
Conductivity	0.03	0.8	0.3

Neutralization Factors (NF): Neutralization Factors (NF) were calculated for different alkaline constituents using the formulae suggested by Khemani L.T. et al.[12]. The general equation used for identifying NF is as follows:

$NF_{(NH4)} = NH_4 / [NO_3] + 2[SO_4]$

$NF_{(Ca)} = Ca / 2[NO_3] + [SO_4]$

$NF_{(Mg)} = Mg / 2[NO_3] + [SO_4]$

The NF values are in the order of Ca (0.74) > Mg (0.31) > NH_4 (0.02), showing that major neutralization is caused by Ca (NF = 0.74) followed by Mg and NH_4. Coarse mode Ca aerosols are contributed by soil dust in the ambient air in India.

Therefore, Ca seems to be the major component for neutralization of rainwater acidity at most of the Indian sites[13,11].

Sequential sampling: During the sampling period, sequential samples were also collected taking 75 ml as a constant volume. Two events in 2010 samples were characterized and collected as sequential samples on 11 and 23 August (Figure-1). In the early portions of rain event, decrease in the pH values was observed sharply in comparison to the later portions of the rain. The concentration of ions also decreases with time. The longest rain event was observed on 11 Aug. for which 5 samples were collected at an interval of 10 min. of total duration of rain event. The decrease in the chemical composition collected during this event is shown in Figure-1. The concentration of Ca was decreased maximum in comparison to other ions during the whole rain event due to their effective washout.

Correlation between ions and factor analysis: Bivariate correlations have been identified to specify the chemical forms of the major ions in rainwater. Table-2 shows the correlation coefficients among these major ions. High correlation coefficients are obtained for the pairs NO_3 and SO_4 (r = 0.71) and Ca and Mg (r = 0.59) indicates that a portion of these may have originated from a similar source. NH_4 was correlated with SO_4 (r = 0.55) indicating the formation of both NH_4HSO_4 and $(NH_4)_2SO_4$.

Table-3 shows the correlation coefficients for anions vs cations combinations. When compared individually, the correlation coefficient of SO_4 with Ca and Mg is 0.85 and 0.74 and of NO_3 with Ca and Mg is 0.57 and 0.66, respectively. But, the correlation coefficient increases when SO_4 was correlated with the sum of Ca and Mg (Ca+Mg) to 0.87, and the coefficient decreases to 0.77 decreases with the addition of K. Similar results were obtained when the sum of anions NO_3 and SO_4 were correlated with the various cation combinations. These results suggest that these ions play an important role in acid neutralization. Factor analysis was conducted to identify the sources of the observed ions. The method used was principle component analysis using SPSS PC package.

The analysis identified two factors. The results are represented in the Table 4. The first factor groups together Ca, Cl, Mg, Na, K, NO_3, SO_4 indicating the significant contribution of soil. The second factor groups together SO_4 and NH_4 indicating the formation of ammonium sulphate which may be formed by reaction of gaseous species[14].

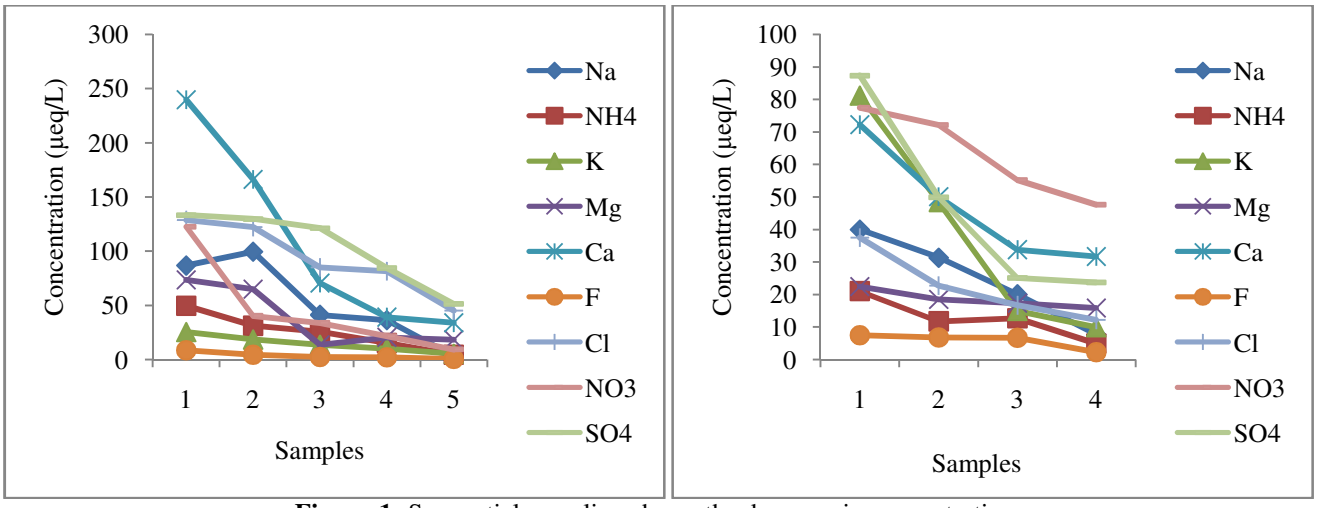

Figure-1: Sequential sampling shows the decrease in concentration.

Table-2: Correlation coefficient of ionic species in rainwater.

	NH_4	Na	K	Mg	Ca	F	Cl	NO_3	SO_4
NH_4	1								
Na	0.53	1							
K	0.47	0.38	1						
Mg	0.30	0.44	0.12	1					
Ca	0.14	0.63**	0.30	0.59*	1				
F	0.44	0.44	0.33	0.47	0.61**	1			
Cl	0.63**	0.78**	0.52	0.42	0.75**	0.68**	1		
NO_3	0.50	0.53	0.23	0.66**	0.55	0.66	0.68**	1	
SO_4	0.55**	0.65	0.08	0.75**	0.73**	0.55	0.69**	0.71**	1

**Correlation is significant ($p < 0.01$).

Table-3: Correlation coefficients for anions vs cations combinations.

	NO_3	SO_4	$(NO_3 + SO_4)$
Ca	0.57	0.85	0.82
Mg	0.66	0.74	0.77
K	0.22	0.16	0.16
NH_4	0.54	0.24	0.35
(Ca+Mg)	0.62	0.87	0.85
(Ca+Mg+K)	0.63	0.77	0.78
$(Ca+Mg+K+NH_4)$	0.64	0.73	0.79
$(K+NH_4)$	0.34	0.13	0.29
$(Ca+Mg+NH_4)$	0.68	0.87	0.87

Table-4: Table showing results of Factor analysis.

Component	Factor 1	Factor 2
Ca	0.81	0.04
Cl	0.88	0.06
Mg	0.76	0.05
Na	0.65	0.02
K	0.55	0.18
NO_3	0.74	0.41
SO_4	0.63	0.58
NH_4	0.19	0.81
Total Variance (%)	68.1	20.5
Eigen values	6.2	2.2
Source	Soil	Secondary aerosols

Conclusion

Rainwater composition was analyzed for their physical and chemical parameters during the monsoon of 2010 at Sikandra (Agra). The pH value indicates the alkaline nature of rainwater. The concentration of cations were greater than anions indicating the dominance if crustal sources. Sequential samples show that the concentration of ions decreases with time.

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