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GK Bagri
Department of Soil Science and Agricultural Chemistry, Institute of Agricultural Sciences, Uttar Pradesh, India

P Raha
Department of Soil Science and Agricultural Chemistry, Institute of Agricultural Sciences, Uttar Pradesh, India

DK Bagri
Krishi Vigyan Kendra, Nagaur-II, Maulasar, Agriculture University, Jodhpur, Rajasthan, India

DL Bagdi
Department of Plant Physiology, S.K.N. College of Agriculture, Jobner, Rajasthan, India

Corresponding Author:
GK Bagri
Department of Soil Science and Agricultural Chemistry, Institute of Agricultural Sciences, Uttar Pradesh, India

Compositional status of cations in rain water of Lanka and Mirzamurad, Varanasi

GK Bagri, P Raha, DK Bagri and DL Bagdi

Abstract
The analysis of rain water samples were carried out in the Department of Soil Science and Agricultural Chemistry Laboratory at the Institute of Agricultural Sciences, Banaras Hindu University, Varanasi during 2015. The rain water samples of two different location *viz.* Lanka and Mirzamurad (Banaras Hindu University, campus), which are relatively free from industrial pollution were examined during south-west monsoon period (July to September) in Varanasi using standardize collection and analytical techniques for evaluation chemical composition of rain water. Magnesium was found in highest amount in comparison to other cations, followed by Ca^{2+}, Na^{+}, K^{+} and NH_4^{+}. Thus, the order of alkali metal cations found in rain water in Varanasi was as follows: $Mg^{2+}>Ca^{2+}>Na^{+}>K^{+}$.

Keywords: Rain water, cations, analytical techniques, chemical composition and Varanasi

Introduction
The increased acidity of rainfall that has been observed in many parts of world may be due to largely to the increase in atmospheric oxides of sulphur and nitrogen from anthropogenic sources. Acid precipitation is also of concern in developing countries as in India where the rainwater is not yet acidic (Subramanian and Saxena, 1980) [3]. Atmospheric NH_3, which is predominantly biogenic in origin, can partially neutralize the acids and cause a decrease in the acidity of rain water, The chemical composition of atmospheric aerosols and particulate matter can also have a market effect on the acidity of precipitation. It has been considered that alkaline dust generated by wind erosion, along with gaseous NH_4 generated by bacterial action in the cultivated lands, can neutralize and thus influence the extent of acid precipitation. Soil in India is, by and large, dusty and rich with basic components like Ca^{2+} and Mg^{2+}, and is the main cause for the observed high levels of aerosols in the atmosphere (Khemani *et al*., 1984) [2]. According to Khemani *et al*. (1984) [2] the phenomenon of acid rain poses no special problem in India, so long as the aerosol state of the air, which is presently alkaline, continues to remain so. However, low pH values in rain water in India, might be restricted to localized regions in highly industrialized cities. An additional factor that is often neglected is the presence of the carbonic acid-bicarbonate buffer system in rain water. The concentration of these buffer components are important in maintaining a pH which is suitable for living organisms and in controlling pH of the rain water at value greater than 5.0. On the other hand, rain water is an important hydrologic input to many forest/agro-ecosystem, but little is known about the chemistry of this form of precipitation. Chemicals carried in such finely dispersed water are deposited directly into leaves and could be a significant factor in vegetative growth, especially at high elevations where forests/commercial crops are often bathed in rain and fog water for long periods. Varanasi is situated on the banks of river Ganga and thus characteristically new alluvial tract. Cropping system in this district is typically rice-wheat, along with some important pockets of vegetables. 80% of annual rainfall in Varanasi and its adjoining district occurs in the summer monsoon season. As agroecologically Varanasi is a semi-arid zone of India, there is high possibility of chemicals carried in finely aerosol in atmosphere could be deposited onto the leaves of crops through rainfall and could be a contributing factor in plant growth. This theme gave the author an impulse to think about the impacts of chemical composition of rainwater in plant growth in this non-industrialized alluvial track of Varanasi district. It has been found from a survey report that although some research works concerning the acid rain and chemical composition of rainwater are available in few parts of India, but there appears to be no systematic investigation on the chemical composition of rain water and it impacts on plant growth in the alluvial tract of Varanasi

district, eastern Uttar Pradesh. Thus it's thought worthwhile to investigate the chemical composition of rain water in Varanasi, U.P. and evaluation of total nutrient inputs in soils through the precipitation. Keeping in view these facts and the importance of the chemical composition in rain water in respect of plant nutrient sources as well as pollutants in atmosphere, this research work was conducted.

Materials and Methods

The analysis of rain water samples were carried out in the Department of Soil Science and Agricultural Chemistry Laboratory at the Institute of Agricultural Sciences, Banaras Hindu University, Varanasi.

Sampling of Rain Water

Rain water was collected in rainy season from three different areas, *viz*. Lanka and Mirzamurad of Varanasi district, Uttar Pradesh. The time schedule for collection of rain water were 25th June to 25th September, 2015 because the normal period of onset of monsoon in this region is the third week of June and it lasts up to the end of the September or sometimes first week of October. At each of the localities three sampling station were placed within 15 kilometers of each other.

Method of Sampling

In Banaras Hindu University, the sample collector was placed about 15 m above the ground level on the roof of Bal Gangadhar Tilak Hostel building. In Lanka and Mirzamurad, collectors were placed about 12 m each above the ground level in an open area, nearest agricultural fields. Each collector had a 19 cm diameter borosilicate glass funnel tightly fitted to a 5L borosilicate glass bottle that remained outdoors to facilitate collection. The method of sampling collected bulk precipitation, including wet and dry deposition. The precipitation samples were then filtered and only aqueous phase was analyzed. The volume of filtrate was measured (range of the rain water volume: from 100 ml to 2300ml). Between two rainfall events the collectors were rinsed by distilled water.

Method of Analysis of Cations in Rain Water

Analysis of Sodium and Potassium in Rain Water

The determinations of Na^+ and K^+ were carried out directly with the flame photometer using appropriate filters and standard solutions were prepared by taking known concentrations of sodium (NaCl) and potassium (KCl).

Analysis of Total Calcium and Magnesium in Rain Water

The total Ca + Mg was determined by complexiметric titration, involving ethylene diamine tetra acetic acid (EDTA). EDTA, under the trade name 'Versenate' or 'Trilon' exhibits strong complexing power with metal ions including alkaline earth metals in an order, depending upon the dissociation constant of the complex. 10 ml of the water sample was pipette out in conical flask. 5 ml of buffer solution (pH 8 to 10) and 5-6 drops of Erichrome Black-T indicator were added and titrated against standard Na-EDTA solution until the colour change from wine red to blue.

Analysis of Calcium in Rain Water

Calcium was also determined by complexiметric titration using murexide indicator. 10 ml of aliquot was taken in conical flask and 2-3 crystals and 5 ml of 16% NaOH solution were added into it. 40-50 mg of murexide indicator powder was added into solution and titrated against 0.01 N EDTA solution till the color gradually changed from orange to reddish violet (purple).

Analysis of Ammonium in Rain Water

The basic method consists of reacting a sample containing NH_4^+ with phenol in presence of oxidizing agents at high pH (11.5-12.0) to form a blue color (Harwood and Kuhn, 1970) [3], the intensity of which is proportional to the concentration of NH4 + in sample.5 ml of sample was pipette out into a 25 ml volumetric flask. 1 ml of EDTA solution (0.01 N) was added in the flask and mixed and allowed the mixture to stand for at least 1 minute. 2 ml of phenol nitropruside reagent was added into it followed by 4 ml of the buffered hypochlorite reagent. After diluting the solution, flasks were placed in water bath, maintained 40 °C and allowed to 30 minutes for color development. The flasks were removed from water bath, cooled at room temperature (10 minutes) and the absorbance of the coloured complex was determined at a wavelength of 636nm against a reagent blank solution NH_4 + concentration in the samples were determined by reference to a standard curve based on analysis of standard working solution of $(NH_4)2SO_4$.

Results and Discussion

Composition of Cations in Rain Water

Results given in Table 1 and 2 presented the concentration of cations *viz*., ammonium, sodium, potassium, calcium and magnesium found in rain water samples from three collection sites in Varanasi during monsoon period and comparative mean values of alkali metal cations in Lanka and Mirzamurad.

Table 1: Composition of cations (mg L^{-1}) in rain water of Lanka.

S. No.	Date of Sampling	NH_4^+	Na^+	K^+	Ca^{2+}	Mg^{2+}
1.	05/07/2015	0.05	**8.2**	1.1	48.0	55.0
2.	07/07/2015	0.05	7.4	1.1	44.0	59.0
3.	08/07/2015	0.18	7.0	0.9	32.0	38.8
4.	09/07/2015	0.15	4.2	0.6	36.0	54.8
5.	10/07/2015	0.07	3.3	0.5	32.0	45.2
6.	11/07/2015	0.05	7.0	1.0	36.0	47.7
7.	15/07/2015	0.12	4.8	0.5	40.0	37.2
8.	16/07/2015	0.20	3.6	0.4	28.0	42.8
9.	23/07/2015	0.05	5.0	0.9	60.0	62.3
10.	24/07/2015	0.05	4.2	0.5	44.0	33.2
11.	01/08/2015	0.08	5.3	1.8	52.0	57.4
12.	02/08/2015	0.11	4.6	1.7	32.0	38.8
13.	09/08/2015	0.06	5.3	1.6	72.0	88.9
14.	10/08/2015	0.06	4.9	1.7	44.0	46.1
15.	17/08/2015	0.12	5.5	1.7	32.0	32.1
16.	21/08/2015	0.06	5.3	0.9	36.0	41.2
17.	22/08/2015	0.06	4.3	1.0	16.0	29.0
18.	29/08/2015	0.22	2.4	0.7	36.0	34.8
19.	30/08/2015	0.06	5.2	0.7	40.0	43.7
Range		0.05-0.20	2.4-8.2	0.5-1.8	16-72	29.0-88.7
Mean		0.09	5.13	1.02	40.0	46.7
S.D. ±		0.05	1.41	0.46	11.9	13.6
Median		0.06	5.00	0.90	36.0	43.7

It was revealed from the data that NH_4^+, Na, K^+, Ca^{2+} and Mg^{2+} were found in all the rain water samples in each location, Mg^{2+} was found in highest amount in comparison to other cations, followed by Ca^{2+}, Na^+, K^+ and NH_4^+. Thus, the order of alkali metal cations found in rain water in Varanasi

was as follows: $Mg^{2+}>Ca^{2+}>Na^{+}>K^{+}$

Table 2: Composition of cations (mg L^{-1}) in rain water of Mirzamurad.

S. No.	Date of Sampling	NH_4^+	Na^+	K^+	Ca^{2+}	Mg^{2+}
1.	06/07/2015	0.06	9.8	2.0	48.0	55.0
2.	07/07/2015	0.18	7.3	1.4	40.0	37.2
3.	08/07/2015	0.06	5.6	1.3	48.0	42.1
4.	10/07/2015	0.07	8.4	1.7	28.0	36.4
5.	11/07/2015	0.07	8.0	0.5	20.0	25.0
6.	16/07/2015	0.21	4.7	0.6	20.0	25.0
7.	17/07/2015	0.06	6.0	0.8	40.0	43.8
8.	21/07/2015	0.05	5.9	0.9	44.0	33.4
9.	24/07/2015	0.07	6.0	0.1	28.0	36.4
10.	31/07/2015	0.05	7.4	0.8	52.0	57.5
11.	03/08/2015	0.05	7.5	0.8	52.0	51.0
12.	04/08/2015	0.05	10.3	1.6	16.0	22.7
13.	08/08/2015	0.06	4.9	0.8	32.0	45.3
14.	09/08/2015	0.13	7.4	1.2	44.0	46.1
15.	16/08/2015	0.05	3.7	0.4	16.0	29.1
16.	17/08/2015	0.07	3.6	0.5	20.0	37.9
17.	18/08/2015	0.06	4.7	0.4	28.0	42.8
18.	26/08/2015	0.07	5.4	0.9	16.0	29.1
19.	30/08/2015	0.53	4.6	0.8	64.0	77.7
Range		0.05-0.53	3.6-10.3	0.1-1.6	16-64	22.7-77.7
Mean		0.10	6.38	0.92	34.5	40.7
S.D. ±		0.11	1.86	0.48	14.3	13.0
Median		0.06	6.00	0.80	32.0	37.9

Tiwari *et al*. (2007) [4]. was also reported same trend of Ca^{2+}, Mg^{2+} and HCO_3^- content domination in rain water of Delhi and adjoining areas. The significant differences of Na+, K+, Ca^{2+} and Mg^{2+} concentration in rain water were found in three locations, whereas NH_4^+ content was very low in all the three locations (0.1 mg L^{-1}). The mean Ca^{2+}, Mg^{2+} and K^+ content was highest in Lanka whereas NH_4^+ and Na^+ were found in Mirzamurad, respectively.

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