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Determination of cations and anions in rain water of Babatpur, Varanasi

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Abstract

The rain water samples were estimated in the laboratory of Soil Science and Agricultural Chemistry Department at the Institute of Agricultural Sciences, Banaras Hindu University, Varanasi during 2015. The rain water samples of Babatpur 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: $\text{Mg}^{2+} > \text{Ca}^{2+} > \text{Na}^+ > \text{K}^+$. The titrimetric techniques were employed for the determination of Cl^- , CO_3^{2-} , HCO_3^- , and NO_3^- and PO_4^{3-} were estimated by colorimetric methods. It was observed that basic anions content (CO_3^{2-} and HCO_3^-) in rain water of Varanasi was found much higher than acidic anions content ($\text{Cl}^- + \text{SO}_4^{2-} + \text{NO}_3^- + \text{PO}_4^{3-}$).

Keywords: Rain water, cations, anions, analytical techniques, chemical composition

Introduction

The mass balance of annual rainfall shows that about 70% is lost by direct evaporation and transpiration by plants, while the remaining 30% goes into the stream flow. The approximate breakup of this stream flow, as consumed by man, is 8% for irrigation, 2% for domestic use, 4% for industries, and 12% for electrical utilities. Irrigation for agricultural purposes and electric power plants are the major consumers of water.

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 agro ecologically 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

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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 tract of Varanasi district.

This survey report indicated 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 its 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 Babatpur 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 15m above the ground level on the roof of Bal Gangadhar Tilak Hostel building. In Babatpur 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 2300 ml). 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 compleximetric titration, involving ethylene diamine tetraacetic 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 color change from wine red to blue.

Analysis of Calcium in Rain Water: Calcium was also determined by compleximetric 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 NH₄⁺ 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 NH₄⁺ concentration in the samples were determined by reference to a standard curve based on analysis of standard working solution of (NH₄)₂SO₄.

Analysis of chloride anion in rain water: The method is based on the titration of a neutral chloride solution with neutral silver nitrate solution in the presence of potassium chromate (K₂CrO₄) indicator. 25 ml aliquot of water sample was taken into a conical flask and 8-10 drops of K₂CrO₄ indicator was added into it. The sample was then titrated against standard 0.05 N AgNO₃ from the burette. At the end point, the color of suspension changed from yellow (due to the presence of CrO₄²⁻ ions) to reddish brown (due to the precipitation of red insoluble Ag₂CrO₄).

Analysis of carbonate and bicarbonate in rain water: The estimation is based on simple acidimetric titration using different indicators which work in alkaline pH range (above 8.2) or in acidic pH (below 6.0 or 4.5). Carbonate and bicarbonate in water can be determined by titrating the water with standard sulphuric acid (0.01 N) using phenolphthalein and later on methyl orange indicator. 10 ml water sample was taken in 100 ml conical flask. 1-2 drops of phenolphthalein was added into it and titrate with standard acid till the pink color just disappeared. The volume of standard acid used was noted. Without discarding the solution, to the colorless solution from the titration (or to the original sample of water if there was no color with phenolphthalein) 1 or 2 drops of methyl orange indicator was added then the titration continued with stirring to the methyl orange end point (yellow) and the final reading was noted.

Analysis of sulphate in rain water: Sulphur was determined turbidimetrically as barium sulphate by method of Massoumi and Cornfield (1963) [3]. 5 ml of water sample was taken in 25 ml volumetric flask. 10 ml of sodium acetate-acetic acid

buffer was added to maintain pH around 4.8, 1 ml of gum acacia and 1 g of BaCl₂ crystal were added into it and shaken well. After volume make up, turbidity of the solution was measured in spectrophotometer at 440 m μ using blue filter. Concentrations of samples were measured from standard curve (K₂SO₄).

Analysis of phosphate in rain water: Phosphate in water was determined calorimetrically by formation of 'molybdenum blue' (Olsen, 1965) [5]. Phosphorus in the water was treated with ammonium molybdate, which formed 'phosphomolybdate' (yellow colour). The phosphomolybdate was reduced by the use of SnCl₂ (a reducing agent). As a result of reduction, some of Mo⁶⁺ was converted to Mo³⁺ and/or Mo⁵⁺, the characteristic blue color. The intensity of the blue color was directly proportional to the quantity of phosphorus. 10 ml of water sample was taken in 25 ml volumetric flask and then the solution was acidified to pH 5.0 by using 2.5 M H₂SO₄. 5 ml of ammonium molybdate solution was added into it and after shaking 1 ml of SnCl₂ solution was added. Volume was made up by distilled water and intensity of the blue color was measured in colorimeter at 660 m μ using red filter.

Analysis of nitrate in rain water: The NO₃⁻ was determined by colorimetrically using a powder mixture of coloring reagents. The powder mixture was prepared by grinding the following reagents: 100 g bariumsulphate + 10 g manganese sulphate monohydrate + 2 g of finely powdered zinc + 75 g of powdered citric acid + 4 g of sulfanilic acid + 2 g of 1-Naphthylamine (Nelson *et al.*, 1954) [5]. 1 ml of water sample was taken in test tube and then 9 ml of acetic acid and 0.3 to 0.5 g powder reagent was added into it. The solution was shaken in centrifuge (4000 rpm) for 50 to 60 Sec. Red color solution was formed the absorbance was measured at 520 m μ . Data obtained from all the observations were statistically analyzed. The S.D. values were evaluated for each chemical parameter of water.

Results and Discussion

Composition of Cations in Rain Water

Results given in Table 1, 2 and 3 presented the concentration of cations viz., ammonium, sodium, potassium, calcium and magnesium found in rain water samples from one collection sites in Varanasi during monsoon period. Comparative mean values of cations and anions in Babatpur are.

Table 1: Composition of cations (mg L⁻¹) in rain water in Babatpur.

S. NO.	Date of Sampling	NH ₄ ⁺	Na ⁺	K ⁺	Ca ²⁺	Mg ²⁺
1.	06/07/2015	0.06	5.1	1.1	76.0	78.5
2.	07/07/2015	0.07	4.0	0.9	72.0	82.5
3.	09/07/2015	0.07	4.6	0.6	80.0	74.5
4.	10/07/2015	0.11	4.8	0.6	40.0	50.1
5.	11/07/2015	0.21	5.9	0.5	96.0	84.3
6.	15/07/2015	0.12	11.9	2.1	48.0	67.9
7.	16/07/2015	0.19	4.4	0.5	44.0	46.1
8.	17/07/2015	0.05	4.1	0.8	28.0	36.4
9.	23/07/2015	0.07	6.2	0.8	36.0	54.1
10.	25/07/2015	0.14	4.8	1.3	48.0	61.5
11.	31/07/2015	0.06	4.7	0.8	44.0	46.1
12.	01/08/2015	0.08	5.9	0.8	80.0	87.4
13.	03/08/2015	0.19	7.5	1.0	124.0	114.2
14.	15/08/2015	0.05	4.9	0.6	112.0	81.2
15.	17/08/2015	0.21	5.0	0.5	56.0	59.9
16.	25/08/2015	0.17	3.8	0.6	48.0	67.2
17.	26/08/2015	0.05	6.0	0.8	52.0	63.9
18.	27/08/2015	0.06	6.4	0.9	52.0	51.0
19.	30/08/2015	0.06	4.7	1.0	68.0	61.8
20.	31/08/2015	0.17	17.4	0.6	148.0	116.0
21.	12/09/2015	0.04	11.2	0.8	64.0	58.3
Range		0.04-0.21	3.8-17.4	0.5-2.1	28-141	36.4-116
Mean		0.11	6.35	0.84	67.4	68.7
S.D. \pm		0.06	3.22	0.35	30.1	20.3
Median		0.07	5.00	0.80	56.0	63.9

The mean range cations in rain water in Varanasi areas were as follow: 0.09 to 0.11 mg L⁻¹ of NH₄⁺, 5.13 to 6.38 mg L⁻¹ of Na⁺, 0.84 to 1.02 mg L⁻¹ of K⁺, 34.53 to 67.43 mg L⁻¹ of Ca²⁺ and 40.71 to 68.7 mg L⁻¹ of Mg²⁺. It was noticed that

maximum contribution of alkali metal ion concentration in rain water of Varanasi was Mg²⁺ (48-50%) and minimum concentration was K⁺ (1%).

Table 2: Composition of anions (mg L⁻¹) in rain water of Babatpur.

S. NO.	Date of Sampling	Cl ⁻	NO ₃ ⁻	SO ₄ ²⁻	PO ₄ ³⁻	CO ₃ ²⁻	HCO ₃ ⁻
1.	06/07/2015	2.84	0.08	0.25	0.35	B.D.L.	414.8
2.	07/07/2015	6.39	0.08	0.28	0.82	B.D.L.	524.6
3.	09/07/2015	2.84	0.06	0.41	0.05	B.D.L.	402.6
4.	10/07/2015	3.55	0.08	0.32	0.35	B.D.L.	402.6
5.	11/07/2015	4.26	0.17	0.08	0.29	B.D.L.	475.8
6.	15/07/2015	4.26	0.07	0.17	0.17	B.D.L.	390.4
7.	16/07/2015	4.26	0.06	0.07	0.11	B.D.L.	329.4
8.	17/07/2015	3.55	0.05	0.32	0.05	B.D.L.	341.6
9.	23/07/2015	3.55	0.07	0.05	0.11	B.D.L.	329.4
10.	25/07/2015	3.55	0.08	0.35	0.11	B.D.L.	305.0
11.	31/07/2015	3.55	0.07	0.05	0.05	B.D.L.	317.2
12.	01/08/2015	2.13	0.07	0.11	0.11	B.D.L.	317.2
13.	03/08/2015	4.26	0.06	0.10	0.17	B.D.L.	463.6
14.	15/08/2015	3.55	0.18	0.19	0.05	288.0	85.4
15.	17/08/2015	3.55	0.10	0.06	0.05	120.0	170.8
16.	25/08/2015	4.26	0.15	0.26	0.11	216.0	321.8
17.	26/08/2015	2.13	0.12	0.10	0.23	192.0	158.6
18.	27/08/2015	3.55	0.08	0.71	0.11	B.D.L.	378.2
19.	30/08/2015	4.26	0.13	0.34	0.29	B.D.L.	317.2
20.	31/08/2015	3.55	0.08	0.15	0.70	B.D.L.	414.8
21.	12/09/2015	4.97	0.06	0.08	0.35	B.D.L.	231.8
Range		2.13-6.39	0.05-0.18	0.05-0.41	0.05-0.82	B.D.L.	85.4-524.6
Mean		3.75	0.09	0.21	0.22	204.0	337.7
S.D. ±		0.91	0.04	0.16	0.20	60.0	105.1
Median		3.55	0.08	0.17	0.11	204.0	329.4

B.D.L. = Below Detectable Level

It was further revealed from mean values of anions in Varanasi that no significant variation in NO₃⁻, SO₄²⁻ and PO₄³⁻ content were recorded in Babatpur.

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