

## Anions Cations Balance in Rainwater of Lanka, Mirzamurad and Babatpur, Varanasi

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Received 5 January 2023, Accepted 12 July 2023, Published on 4 September 2023

### ABSTRACT

The analysis of anions cations balance in rainwater 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 rainwater samples of three different location viz. Lanka, Mirzamurad and Babatpur places of BHU, Varanasi, which are relatively free from industrial pollution were examined during south-west monsoon period (July to September) in Varanasi using standardize selection and analytical methods for evaluation of anions cations balance of rainwater. It was revealed from the Tables 1-3 that the total mineralization varied from 53.65 to 171.38 mg L<sup>-1</sup> in Lanka, 25.49 to 153.55 mg L<sup>-1</sup> in Mirzamurad and 73.32 to 286

mg L<sup>-1</sup> in Babatpur, respectively. In an average total mineralization was highest in Babatpur followed by Lanka and Mirzamurad.

**Keywords** Anions-Cations Balance, Rainwater, Lanka, Mirzamurad, Babatpur.

### INTRODUCTION

Water that is potable (drinkable) should be electrically neutral. This is investigated by taking into account results from the following analytical methods: pH, conductivity, total dissolved solids, and other analytical tests that identify main cationic and anionic constituents. Ratios are looked at between calculated results and actual analytical results. When outcomes are beyond of the expected ranges, reinvestigation is must to bring the CA Balance closer to neutral (which may not be possible). Laboratories use the CA Balance to determine if they have conducted their analytical testing correctly. If water is potable then the CA Balance is a good way to verify that the laboratory testing was done well as long as our report includes the above testing protocols. If testing water is not potable then the CA Balance is more useful the cleaner the water you submitted is. If your water is contaminated, then there is no analytical cause for reporting or conducting a CA Balance. It is important because many analytical reports will provide CA Balance results. Most people do not understand that the CA Balance is really only useful when looking

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at pristine water. Standard procedures discuss a 5% acceptable/working range for potable waters. SVL uses guidelines around 10% to help us with testing semi-clean waters.

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 sulfur and nitrogen from anthropogenic sources. Acid precipitation is also of concern in developing countries as in India where the rainwater is not yet acidic. Atmospheric  $\text{NH}_3$ , which is predominantly biogenic in origin, can partially neutralize the acids and cause a decrease in the acidity of rainwater, The chemical constituents of atmospheric aerosols and particulate matter can also have a market effect on the acidity of precipitation. It has been considered that alkali dust collected by wind erosion, along with gaseous  $\text{NH}_4$  generated by bacterial action in the cultivated lands, can neutralize and thus affected part of acid precipitation. Soil in India is, by and large, dusty and rich with basic components like  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ , and is the main cause for the observed high levels of aerosols in the atmosphere. Keeping in view these facts this investigation was carried out to know the Anions cations balance in rainwater of Lanka, Mirzamurad and Babatpur, Varanasi.

## MATERIALS AND METHODS

The analysis of rainwater samples was completed in the Department of Soil Science and Agricultural Chemistry Laboratory at the Institute of Agricultural Sciences, BHU, Varanasi.

**Sampling of rainwater:** Rainwater was collected in rainy season from three different areas, viz. Lanka, Mirzamurad and Babatpur of Varanasi district, Uttar Pradesh. The time schedule for collection of rainwater were 25<sup>th</sup> June to 25<sup>th</sup> 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:** The samples collector was placed about 15 m above the soil level on the roof of

Bal Gangadhar Tilak Hostel building. In Lanka and Mirzamurad, collectors were placed about 12m each above the ground level in an open area, nearest agricultural fields. Each collector had a 19cm 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 precipitated samples were filtered and only aqueous phase was analyzed. The volume of filtrate was measured (range of the rainwater volume: from 100 ml to 2300 ml). Between two rainfall events the collectors were rinsed by distilled water.

**Estimation of pH in rainwater:** The pH was measured with a digital pH meter using reference (KCl) and glass electrodes standardized with pH 4.0 and pH 9.2 reference buffers before and after pH determinations. Since pH is influenced by extreme values of rainfall amount, rainfall weighted mean values of pH were used instead of arithmetic means.

**Estimation of EC in rainwater:** Electrical conductivity is used for determination of total concentration of soluble salts or ionized constituents in water. It is related to the sum of cations and anions as determined chemically. The EC was measured with conductivity bridge using standard potassium chloride solution for calibration and determination of cell constant. Since EC is influenced by temperature, maintenance of temperature is important on account of the fact that specific conductance is increased by 2% per degree centigrade rise of temperature. The temperature in water samples were maintained in water bath at 25°C.

## Method of analysis of cations in rainwater

**Method of analysis of sodium and potassium in rainwater:** The determinations of  $\text{Na}^+$  and  $\text{K}^+$  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).

**Method of analysis of total calcium and magnesium in rainwater:** The total Ca + Mg was determined by complexometric titration, involving ethylene diamine tetra-acetic acid (EDTA). EDTA, under the

trade name 'Versenate' or 'Trilon' exhibits more complexing power with metal ions including alkali 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 ammonium in rainwater:** The basic method consists of reacting a sample containing  $\text{NH}_4^+$  with phenol in presence of oxidizing agents at high pH (11.5-12.0) to form a blue color (Harwood and Kuhn 1970), the intensity of which is proportional to the concentration of  $\text{NH}_4^+$  in sample. Five ml of sample was taken into a 25 ml volumetric flask. 1 ml of EDTA solution (0.01N) 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  $40^\circ\text{C}$  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 colored complex was determined at a wavelength of 636 nm against a reagent blank solution.  $\text{NH}_4^+$  concentration in the samples were determined by reference to a standard curve based on analysis of standard working solution of  $(\text{NH}_4)_2\text{SO}_4$ .

#### Method of analysis of anions in rainwater

**Analysis of chloride anion in rainwater:** This method is based on the titration of a neutral chloride solution with neutral silver nitrate solution in presence of potassium chromate ( $\text{K}_2\text{CrO}_4$ ) indicator. 25 ml aliquot of water sample was taken into a flask and 8-10 drops of  $\text{K}_2\text{CrO}_4$  indicator was added into it. The sample was then titrated against standard 0.05N  $\text{AgNO}_3$  from the burette. At the end point, the color of suspension changed from yellow (with the presence of  $\text{CrO}_4^{2-}$  ions) to reddish brown (due to the precipitation of red insoluble  $\text{Ag}_2\text{CrO}_4$ ).

**Analysis of sulphate in rainwater:** Sulfur was estimated turbidimetrically as barium sulphate by pro-

cedure of Massoumi and Cornfield (1963). Five ml of water sample was added in 25 ml volumetric flask. 10 ml of sodium acetate-acetic acid buffer was added to maintain pH around 4.8, 1ml of gum acacia and 1g of  $\text{BaCl}_2$  crystal were added into it and shaken well. After volume make up, turbidity of the solution was measured in spectrophotometer at 440m $\mu$  using blue filter. Concentrations of samples were measured from standard curve ( $\text{K}_2\text{SO}_4$ ).

**Analysis of phosphate in rainwater:** Phosphate in water was determined calorimetrically by formation of 'molybdenum blue' (Olsen *et al.* 1965). Phosphorus in the water was treated with ammonium molybdate, which formed 'phosphomolybdate' (yellow color). The phosphomolybdate was reduced by the use of  $\text{SnCl}_2$  (a reducing agent). Due to result of reduction, some of  $\text{Mo}^{6+}$  was converted to  $\text{Mo}^{3+}$  and/or  $\text{Mo}^{5+}$ , the characteristic blue color. The intensity of blue color was directly proportional to the quantity of phosphorus. 10 ml of water sample was taken in 25ml volumetric flask and then the solution was acidified to pH 5.0 by using 2.5M  $\text{H}_2\text{SO}_4$ . 5 ml of ammonium molybdate solution was added into it and after shaking 1ml of  $\text{SnCl}_2$  solution was added. Volume was made up by distilled water and intensity of the blue color was measured in colorimeter at 660 m $\mu$  using red filter.

**Analysis of nitrate in rainwater:** The  $\text{NO}_3^-$  was determined by calorimetrically using a powder mixture of coloring reagents. The powder mixture was prepared by grinding the following reagents: 100g barium sulphate + 10g manganese sulphate monohydrate + 2g of finely powdered zinc + 75g of powdered citric acid + 4g of sulfanilic acid + 2g of 1-Naphthylamine (Nelson *et al.* 1954). One ml water sample was taken in test tube and then 9 ml of acetic acid and 0.3 to 0.5g powder reagent was added into it. The solution was shaken in centrifuge (4000rpm) for 50 to 60 Second. Red color solution was formed the absorbance was measured at 520 m $\mu$ . Data obtained from all the observations were statistically analyzed. The SD values were evaluated for each chemical parameter of water.

**Statistical analysis:** Data obtained from all observations were statistically calculated by SPSS.

**Table 1.** Anion-cation balance along with pH and EC of the rainwater of Lanka..

Sl. No.	Date of sampling	mg L <sup>-1</sup>			$\Sigma^{-}-\Sigma^{+}$	Anions cations	pH	EC (dSm <sup>-1</sup> )
		Total anions Cl <sup>-</sup> +SO <sub>4</sub> <sup>2-</sup> + NO <sub>3</sub> <sup>-</sup> +PO <sub>4</sub> <sup>3-</sup> = $\Sigma^{-}$	Total cations NH <sub>4</sub> <sup>+</sup> + Na <sup>+</sup> + K <sup>+</sup> + Ca <sup>2+</sup> + Mg <sup>2+</sup> = $\Sigma^{+}$	Total mineral <sup>+</sup> ization $\Sigma^{-}+\Sigma^{+}$				
1	05/07/2015	4.57	112.35	116.92	-107.78	0.04	7.6	0.15
2	07/07/2015	3.89	111.55	115.44	-107.66	0.03	8.8	0.02
3	08/07/2015	3.87	78.88	82.75	-75.01	0.05	8.2	0.02
4	09/07/2015	3.19	95.75	98.94	-92.56	0.03	7.8	0.03
5	10/07/2015	3.77	81.07	84.84	-77.3	0.05	8.6	0.04
6	11/07/2015	4.76	91.75	96.51	-86.99	0.05	8.6	0.04
7	15/07/2015	4.11	82.62	86.73	-78.51	0.05	8.3	0.02
8	16/07/2015	3.38	75	78.38	-71.62	0.05	8.2	0.01
9	23/07/2015	3.93	128.25	132.18	-124.32	0.03	8.1	0.04
10	24/07/2015	3.87	81.95	85.82	-78.08	0.05	8.2	0.04
11	01/08/2015	4.27	116.58	120.85	-112.31	0.04	7.9	0.04
12	02/08/2015	2.82	77.21	80.03	-74.39	0.04	7.2	0.05
13	09/08/2015	3.52	167.86	171.38	-164.34	0.02	8.1	0.05
14	10/08/2015	4.27	96.76	101.03	-92.49	0.04	8.0	0.04
15	17/08/2015	5.34	71.42	76.76	-66.08	0.07	7.6	0.05
16	21/08/2015	4.95	83.46	88.41	-78.51	0.06	7.6	0.05
17	22/08/2015	3.29	50.36	53.65	-47.07	0.07	7.6	0.13
18	29/08/2015	4.6	74.12	78.72	-69.52	0.06	8.0	0.13
19	30/08/2015	3.97	89.66	93.63	-85.69	0.04	8.0	0.07

## RESULTS AND DISCUSSION

### Ionic balance and electrochemical properties of rainwater

The concentration of total anions (Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup> and PO<sub>4</sub><sup>3-</sup>) and total cations (NH<sub>4</sub><sup>+</sup>, Na<sup>+</sup>, K<sup>+</sup>, Ca<sup>2+</sup> and Mg<sup>2+</sup>), the values of total mineralization (anions and cations) in mg L<sup>-1</sup>, pH and electrical conductivity (EC) values are given in Tables 1-3 for Lanka, Mirzamurad and Babatpur, respectively. The concentration of CO<sub>3</sub><sup>2-</sup> and HCO<sub>3</sub><sup>-</sup> in rainwater are not considered for total mineralization as these ions are acting as buffering ions in rain water.

It was revealed from the Tables 2-3 that the total mineralization varied from 53.65 to 171.38 mg L<sup>-1</sup> in Lanka, 25.49 to 153.55 mg L<sup>-1</sup> in Mirzamurad and 73.32 to 286 mg L<sup>-1</sup> in Babatpur, respectively. In an average total mineralization was highest in Babatpur followed by Lanka and Mirzamurad. Components such as H, NH<sub>4</sub>, Ca, SO<sub>4</sub>, NO<sub>3</sub>, F, Pb, Fe, Mn and Al are assumed to be mainly emitted from sources on land, whereas Na, Mg and Cl originate mainly from

sea spray, K is emitted by land and sea sources (Naik *et al.* 2002) but in case of Varanasi, all the above-mentioned analyzed components are assumed to be mainly emitted from land. The rainwater samples in Varanasi were collected mainly in cultivated areas, specifically Babatpur and Mirzamurad areas is totally agricultural belt viz., rice-wheat cropping system along with some vegetable cultivation. Babatpur areas are exposed to continuous tillage operation and possibilities of the emission of above-mentioned components (cations and anions) through soil particles from the land are enhanced, which reflect on total mineralization (73.32 to 286 mg L<sup>-1</sup>) in rainwater of Varanasi. Furthermore, total cations concentration in rainwater was dominated over the total anions' concentration, thus the values of the ratio of anions/cations was found very low.

The anion-cation balance (mg L<sup>-1</sup>) in rainwater at the three stations with pH values are also given in Tables 1-3. The pH in rainwater is assumed to be characterized by a difference between the anion and cation sums ( $\Sigma^{-}-\Sigma^{+}$ ). If the difference is positive, the rainwater is acidic and if it is negative, the rainwater is alkaline. Examinations of the values of difference

**Table 2.** Anion-cation balance along with pH and EC of the rainwater of Mirzamurad.

Sl. No.	Date of sampling	mg L <sup>-1</sup>			$\Sigma^{-}-\Sigma^{+}$	Anions cations	pH	EC (dSm <sup>-1</sup> )
		Total anions Cl <sup>-</sup> +SO <sub>4</sub> <sup>2-</sup> + NO <sub>3</sub> <sup>-</sup> +PO <sub>4</sub> <sup>3-</sup> = $\Sigma^{-}$	Total cations NH <sub>4</sub> <sup>+</sup> + Na <sup>+</sup> + K <sup>+</sup> + Ca <sup>2+</sup> + Mg <sup>2+</sup> = $\Sigma^{+}$	Total mineral ization $\Sigma^{-}+\Sigma^{+}$				
1	06/07/2015	6.17	114.86	121.03	-108.69	0.05	7.8	0.04
2	07/07/2015	3.73	86.08	89.81	-82.35	0.04	8.0	0.03
3	08/07/2015	4.62	97.06	101.68	-92.44	0.05	8.2	0.03
4	10/07/2015	5.23	74.57	79.8	-69.34	0.07	7.9	0.06
5	11/07/2015	5.3	53.57	58.87	-48.27	0.10	8.2	0.03
6	16/07/2015	4.06	50.51	54.57	-46.45	0.08	8.0	0.04
7	17/07/2015	4.06	90.66	94.72	-86.6	0.04	8.1	0.05
8	21/07/2015	4.51	84.25	88.76	-79.74	0.05	7.8	0.04
9	24/07/2015	3.29	70.57	73.86	-67.28	0.05	7.7	0.04
10	31/07/2015	4.64	117.75	122.39	-113.11	0.04	7.9	0.15
11	03/08/2015	4.06	111.35	115.41	-107.29	0.04	8.0	0.11
12	04/08/2015	4.24	50.65	54.89	-46.41	0.08	8.1	0.12
13	08/08/2015	4.04	83.06	87.1	-79.02	0.05	8.0	0.13
14	09/08/2015	6.3	98.83	105.13	-92.53	0.06	7.9	0.14
15	16/08/2015	3.24	49.25	52.49	-46.01	0.07	8.0	0.09
16	17/08/2015	4.62	62.07	66.69	-57.45	0.07	8.2	0.16
17	18/08/2015	4	75.96	79.96	-71.96	0.05	7.7	0.12
18	26/08/2015	4.33	51.47	55.8	-47.14	0.08	7.9	0.18
19	30/08/2015	5.92	147.63	153.55	-141.71	0.04	7.6	0.13

between anions and cations sums indicate that all the values in three locations were negative. This feature is further examined by the evaluation of values of anion and cations in Tables 1-3, which also revealed that cations were in excess in rainwater. Thus, pH values varied from 7.2 to 8.8 in Lanka, 7.6 to 8.2 in Mirzamurad and 7.6 to 8.5 indicating that rainwater in Varanasi was neutral to alkaline range. Excess cation i.e., 47.0 to 164.3 mg L<sup>-1</sup> in Lanka, 46.0 to 141.7 mg L<sup>-1</sup> in Mizamurad and 65.3 to 277.6 mg L<sup>-1</sup> in Babatpur, which were in alkaline nature, mainly responsible for the observed alkaline pH in rainwater samples. Calcium, magnesium, sodium and chloride ions were dominated at all the three locations in Varanasi, other ions measured were mostly present in very low concentrations. The alkaline pH values observed in Varanasi may be due to the influence of dust particles suspended in the atmosphere. These dust particles are rich in calcium/magnesium bicarbonate/carbonate which is the major buffering agent for rainwater. Due to the highly alkaline nature of soil in Northern India, the role of HCO<sub>3</sub><sup>-</sup> concentration was observed very high in all the three locations of Varanasi, but the EC were noticed less than 0.2 dSm<sup>-1</sup>. Hydrogen ion concentration increased 4 times from west to

east across northern Minnesota (United States) as the effect of alkaline dust (Ca<sub>2</sub><sup>+</sup> + Mg<sub>2</sub><sup>+</sup>) decreased 2 to 3 times. A considerable part of H<sup>+</sup> ion concentration in rainwater in Hungary, is neutralized mainly by soil derived Ca components. The concerned high pH data of rainwater have been attributed to the dominance of crustal components or suspended particulate matter rich in particularly carbonates and bicarbonates of Ca<sub>2</sub><sup>+</sup> which buffer the acidity of sulphate and nitrate, which is commonly observed under Indian subcontinent (Budhavant *et al.* 2011). In general, other neutralizing capacity of cations are Mg<sub>2</sub><sup>+</sup>, NH<sub>4</sub><sup>+</sup> and K<sup>+</sup>. The Ca<sub>2</sub><sup>+</sup> aerosols seem to be a major component for neutralization of rainwater acidity at most of the Indian sites. In view of the above facts and in light of the this investigation, it is confirmed that the alkaline properties of the particulate matter in rainwater are responsible for neutralizing the acidic ions and consequently for the observed increase in pH. The cations are mainly of soil origin and predominantly present in giant size range. They are, therefore washed out with greater efficiency under conditions of highest rainfall category i.e., >30 mm than the anions which are mainly in the sub- $\mu$ m size range.

**Table 3.** Anion-cation balance along with pH and EC of the rainwater of Babatpur.

Sl. No.	Date of sampling	mg L <sup>-1</sup>			$\Sigma^{-}-\Sigma^{+}$	Anions cations	pH	EC (dSm <sup>-1</sup> )
		Total anions Cl <sup>-</sup> +SO <sub>4</sub> <sup>2-</sup> + NO <sub>3</sub> <sup>-</sup> +PO <sub>4</sub> <sup>3-</sup> = $\Sigma^{-}$	Total cations NH <sub>4</sub> <sup>+</sup> +Na <sup>+</sup> + K <sup>+</sup> +Ca <sup>2+</sup> + Mg <sup>2+</sup> = $\Sigma^{+}$	Total mineral ization $\Sigma^{-}+\Sigma^{+}$				
1	06/07/2015	3.52	160.76	164.28	-157.24	0.02	7.6	0.05
2	07/07/2015	7.57	159.47	167.04	-151.9	0.05	7.7	0.04
3	09/07/2015	3.36	159.77	163.13	-156.41	0.02	8.1	0.04
4	10/07/2015	4.3	95.61	99.91	-91.31	0.04	8.5	0.06
5	11/07/2015	4.8	186.91	191.71	-182.11	0.03	8.5	0.08
6	15/07/2015	4.67	130.02	134.69	-125.35	0.04	7.9	0.14
7	16/07/2015	4.5	95.19	99.69	-90.69	0.05	8.1	0.08
8	17/07/2015	3.97	69.35	73.32	-65.38	0.06	7.9	0.05
9	23/07/2015	3.78	97.17	100.95	-93.39	0.04	8.1	0.06
10	25/07/2015	4.09	115.74	119.83	-111.65	0.04	7.9	0.04
11	31/07/2015	3.72	95.66	99.38	-91.94	0.04	7.8	0.08
12	01/08/2015	2.42	174.18	176.6	-171.76	0.01	8.0	0.06
13	03/08/2015	4.59	246.89	251.48	-242.3	0.02	7.8	0.07
14	15/08/2015	3.97	198.75	202.72	-194.78	0.02	7.9	0.09
15	17/08/2015	3.76	121.61	125.37	-117.85	0.03	8.2	0.08
16	25/08/2015	4.78	119.77	124.55	-114.99	0.04	8.0	0.04
17	26/08/2015	2.58	122.75	125.33	-120.17	0.02	8.1	0.03
18	27/08/2015	4.45	110.36	114.81	-105.91	0.04	7.8	0.06
19	30/08/2015	5.02	135.56	140.58	-130.54	0.04	7.6	0.05
20	31/08/2015	4.48	282.17	286.65	-277.69	0.02	7.9	0.08
21	12/09/2015	5.46	134.34	139.8	-128.88	0.04	8.0	0.06

Furthermore, the ionic deposition of plant nutrients (i.e., NO<sub>3</sub><sup>-</sup>+NH<sub>4</sub><sup>+</sup>, PO<sub>4</sub><sup>3-</sup>, K<sup>+</sup>, SO<sub>4</sub><sup>2-</sup>, Ca<sub>2</sub><sup>+</sup>, Mg<sub>2</sub><sup>+</sup>, Cl<sup>-</sup>) with precipitation is an important aspect of rainwater chemistry. Considerable amount of nutrient ions (both primary and secondary) in rainwater suggest that impact of rainwater on vegetation may be an important mechanism for nutrient inputs. Generally, these inputs have been ignored when most nutrient budgets reported in the literature were constructed. It is an important hydrologic input to the cultivated areas and could be a significant factor in plant growth. The total deposition of the individual ion depends on its concentration in atmosphere and the amount of rainfall.

#### ACKNOWLEDGMENT

The realization of this experiment is thanks to all authors whose works are consulted and Department of Soil Science and Agricultural Chemistry, Institute

of Agricultural Sciences, Banaras Hindu University, Varanasi for providing all the facilities to complete analysis work are equally acknowledged.

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