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Cations chemistry characterization of Rainwater of the Varanasi district in the indo-gangetic plains, India

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Abstract
The chemical composition of rainwater is good indicators of the air pollution with rapid economic developing; air quality has greatly changed in Varanasi. To investigate Chemical feature of precipitation and atmospheric pollution characteristics. The current study was aimed to assess the different cationic concentrations in rain water of Varanasi. Rain waters samples were collected in rainy season from roof of the Bal Gangadhar Tilak Hostel at Banaras Hindu University, the samples were collected in pre-cleaned and sterilized polyethylene bottles of two litre capacity. All collected samples were analyzed for major cations using APHA (1992) [1] procedure and suggested precautions were taken to avoid contamination. The various parameters determined were pH, EC (electrical conductivity), calcium (Ca^{2+}), magnesium (Mg^{2+}), pH and EC were determined by pH, conductivity meter, $Ca^{2+,}$ Mg^{2+}, were estimated by titrimetric. The order of basic cations (mean) found in rain water of Varanasi was as follows: $Na^{+}>Mg^{2+}>K^{+}>Ca^{2+}$.

Keywords: rainwater, cations**,** indo-gangetic plains, chemical composition

Introduction
Urbanization is a process which involves economic and industrial development and consequently population growth. This in turn leads to higher energy production and consumption, resulting in problems related to air pollution. According to Fenger (1999) [2] and Cao *et al.* (2011) [3], air pollution is a major problem in urban areas due to emissions from transportation and the interaction of air pollutants originating from a variety of sources and may have a significant effect on the environment Concentrations of many compounds present in the atmosphere have been significantly affected by human activities such as industry, agriculture, burning of vegetation and fossil fuel (Nègrel and Roy, 1998; Kohler *et al*, 1997) [7, 5]. Quantification of these changes and their effect on terrestrial and aquatic ecosystems is important because of their potential adverse effects (Nriagu and Davidson, 1986) [6]
Rainwater functions as a major sink for both gaseous and particulate matter including trace metals in the atmosphere and therefore plays an important role in controlling the concentrations of these species. Scavenging of the atmospheric pollutants by rain affects the chemical composition and the pH of rainwater. The degree of acidity in rainwater depends on the neutralization effects of certain components such as ammonia and calcium carbonate and/or hydroxide on the acidic ions present in the water (Kulshrestha *et al*., 1995a, b) [7]. Determination of rainwater composition reveals the relative importance of the different sources/types of gases and particulate matter present in the atmosphere.
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. 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 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 Chemicals present in the

atmosphere influence the chemical characteristics of rainwater whereas the material deposited by the rain affects soil, surface water and vegetation. Previous studies on the chemical composition of rainwater (Galloway *et al*., 1987, Larssen *et al*., 1999, Larssen and Carmichael, 2000, Feng *et al*., 2001, Tang *et al*., 2005) [8-12] have revealed that the composition of rainwater depends on the local emission, pollutants transport, sea level elevation and drop size, which in turn influences the rainout (incloud scavenging) and the washout (below-cloud scavenging). Climatic conditions may also affect the levels of trace substances in rainwater. Over the last 20 years, rainwater chemistry has been subjected to intense research and many studies on the chemical composition, long and short-term trends of precipitation have been conducted worldwide (Tu *et al*., 2005, Rogora *et al*., 2004, Sickles and Grimm, 2003, Avila and Roda, 2002, Seto *et al*., 2002, Loye-Pilot *et al*., 1986) [13-18]. Monitoring the chemical nature of rainwater in India is even more important due to the rapid growth in industrialization, intensive chemical usage in manufacturing processes, despite the possible environmental consequences of wet deposition.

Rainwater composition plays an important role in scavenging soluble components (particulate matter, organic and inorganic gaseous pollutants) from the atmosphere and helps us to understand the relative contribution of different sources of atmospheric pollutants (Kulshrestha *et al*. 2003) [19]. The composition of rainwater actually reflects the composition of the atmosphere through which it falls. Also, the study of composition of wet deposition encourages in evaluating the relative importance of different sources for gases and particulate matters (Demirak *et al*. 2006) [20]. Increasing 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) [22]. 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) [23]. According to Khemani *et al*. (1984) [24] 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 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. The present study reports the chemical composition of precipitation in Varanasi. The objective of the present study is to examine the level of atmospheric pollution in rainwater through the determination of chemical composition of rainwater.

Geographical Description

Geographically the district Varanasi is situated at $25^0$18' of Northern latitude, 83^0 03' of Eastern longitude and at an altitude of 128.83 m above the mean sea level in the Indo-Gangatic plain of eastern Uttar Pradesh. The district Varanasi having alluvial soil lies in semi-arid region to sub humid belt of Northern India. The mean annual precipitation is 1100 mm. The area occasionally experiences winter cyclonic rain during December to February. In term of percentage of total rainfall, about 84% is received from June to September, 0.7% October to December, 6% from January to February and 9.3% from March to May as pre monsoonic rain. The mean relative humidity of this area is about 68% with maximum 82% and minimum 30% during July to September and April to early June, respectively. The minimum and maximum average temperature of the area range from 4.4^0 to 28.2 ^{0}C, respectively. The temperature begins to rise from February onward until the summer often exceeding 45 ^{0}C in the month of May and June. During these extremely hot months desiccating winds blow from west to east and dust storm frequently occurs.

Materials and Methods

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

Collection and Sampling Method of Rain Water

Rain water samples were collected in rainy season from roof of the Bal Gangadhar Tilak Hostel, Banaras Hindu University, Varanasi, Uttar Pradesh, during 15th June to 15th October. The global position of the rain water collection point was $25^0$16.154' of Northern latitude and $82^0$59.190' of eastern latitude. The samples were collected in different days in the rainy season period. In Banaras Hindu University, the sample collector was placed about 25 m above the ground level on the roof of Bal Gangadhar Tilak Hostel building. Rainwater collector consists of a polypropylene funnel (20 cm in diameter) with a 2-l polypropylene bottle (Tiwari *et al*. 2012) [24]. For prevention of any type of contaminations, the

collector was washed with triple distilled water daily morning and evening and also before installation of new bottle and after the collection of each sample. Immediately after collection, Thymol (<5 mg) was added to precipitation samples to avoid any changes due to biological degradation. From the collected samples, a small portion was used for pH and electrical conductivity measurements, which is drained after the measurement. Field blank was also collected and analyzed as rainwater samples.

Determination of Electrochemical Properties of Rainwater

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 determination. Since pH is influenced by extreme values of rainfall amount, rainfall weighted mean values of pH were used instead of arithmetic means. The 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 E.C. of water was measured with Conductivity Bridge using standard potassium chloride solution for calibration and determination of cell constant. Since it 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 ^{0}C.

Determination of Ions Chemistry of Rainwater

Methods of Sodium and Potassium Estimation of Rainwater

The determinations of Na^+ and K^+ were carried out directly with the flame photometer using appropriate filters and standard prepared by taking known concentration of sodium (NaCl) and potassium (KCl). The standard curve of Na^+ and K^+ were separately drawn by plotting flame photometer reading Y-axis and Na^+ and K^+ solution (mgL^{-1}) on X-axis. The concentration of Na^+ and K^+ in the unknown sample was read from the curve.

Methods of Total Calcium and Magnesium Estimation of Rainwater

The total Ca^{2+} + Mg^{2+} was determined by complex metric titration, involving ethylene diamine tetra acetic acid (EDTA). EDTA, under the trade name 'Versenate' or Trilon exhibit as 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 (NH_4OH + NaCl) solution (pH 8 to 10) and 5-6 drops of Erichrome Black-T indicator were added and titrated against standard EDTA solution until the colour changes from wine red to blue.

Calcium Estimation in Rainwater

Calcium was determined by complex metric titration using murexide indicator. 10mL 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 solutions till the colour gradually changed from orange to reddish violet (Purple).

Results and Discussion

The chemical composition of rain is known to be influenced by various meteorological factors such as wind direction, rainfall rate, total amount of rainfall and the height of the cloud base. Chemicals carried in finely aerosol in atmosphere could be deposited onto leaves of crops, water bodies, Soil surface through rainfall and could be a significant factor in vegetative growth of crops in agriculture as well as forests and consequently influence the health of human and livestock.

Electrochemical Characterization of Rain Water

The data on important electrochemical properties of rain water, *viz.*, pH and EC of Varanasi have been presented in the Table 1. The rain water samples collected from Varanasi have shown pH values ranging from 6.5-8.2. Thus, rain water in Varanasi observed mostly neutral to alkaline, Electrical conductivity of rain water of Varanasi was observed from 0.002-0.150 dSm^{-1}.

Cations Chemistry of Rain Water

Results given in Table 1 presented the concentration of cations, *viz.*, sodium, potassium, calcium and magnesium in rain water samples of Varanasi during South West monsoon period and comparative mean values of are shown in Fig. 1. It was revealed from the data that K^+ and Mg^{2+} were found in all the rain water samples. The Na^+ and Ca^{2+} were found only in 56.1% and 10.5%, respectively in rain water samples. The order of basic cations (mean) found in rain water of Varanasi was as follows: $Na^+ > Mg^{2+} > K^+ > Ca^{2+}$. The mean value of total basic cations ($Na^+ + K^+ + Ca^{2+} + Mg^{2+}$) was found 2.42 meq L^{-1}). Thus, neutralization of acidic anions (*viz.*, Cl^-, $SO_4^=$ etc.) by basic anions ($CO^=_3$ and HCO^-_3) was noticed in samples. The alkaline properties of the particulate matter in rain water were 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. The range of cations in rain water of Varanasi were as follows: 0.00-1.35 meq L^{-1} of Na^+, 0.08-0.51 meq L^{-1} of K^+, 0.0-5.8 meq L^{-1} of Ca^{2+} and 0.0-2.7 meq L^{-1} of Mg^{2+}. Thus, higher range of Ca^+ and Mg^+ in rain water were observed in rain water were noticed in Varanasi. +. It was noticed that maximum contribution of alkali metal ion concentration in rain water of Varanasi was Ca^{2+} and minimum concentration was K^+. The principal cations present in rain water are Ca^{2+}, Mg^{2+}, Na^+ and K^+. The alkali hazard involved in the use of water for irrigation determine the absolute and relative concentration of the cations. If the proportion of sodium is high, the alkali hazard is high. If the calcium and magnesium is high, the hazard is low. The Sodium Adsorption Ratio (SAR) of a solution or water is related to the adsorption of sodium by the soil. Where all ionic concentration is expressed in meq L^{-1}. It was revealed from Table 1 that SAR values of rain water in Varanasi varied from 0.0-3.5. It was noticeable that SAR values were < 10 and EC were < 2.0 d Sm^{-1} in all the samples of the rain water. Thus, this rain water in Varanasi is suitable for safe irrigation, without any sodicity problems.

Table 1: Concentration of Cations in Rainwaters of Varanasi ($meqL^{-1}$)

S. N	Date	pH	EC	Na^{+}	K^{+}	Ca^{++}	Mg^{++}	SAR
1	14/06/2008	7.3	0.011	0.00	0.49	0.00	1.40	0.0
2	15/06/2008	7.6	0.010	0.00	0.31	0.00	0.03	0.0
3	16/06/2008	7.6	0.110	0.00	0.49	0.00	1.20	0.0
4	18/06/2008	7.2	0.033	0.04	0.28	0.00	1.10	0.1
5	19/06/2008	8.2	0.150	0.04	0.13	0.00	0.99	0.0
6	21/06/2008	7.3	0.163	0.13	0.08	0.00	0.95	0.2
7	22/06/2008	7.7	0.130	0.00	0.41	0.00	1.40	0.0
8	23/06/2008	7.6	0.128	0.00	0.33	0.00	1.40	0.0
9	24/06/2008	7.1	0.029	0.00	0.26	0.00	0.47	0.0
10	28/06/2008	7.3	0.071	0.04	0.31	0.00	1.40	0.0
11	29/06/2008	7.1	0.037	0.13	0.36	0.00	1.20	0.3
12	30/06/2008	6.9	0.043	0.09	0.33	0.00	0.62	0.2
13	01/07/2008	7.1	0.018	0.00	0.41	0.00	2.00	0.0
14	02/07/2008	7.2	0.017	0.00	0.41	0.00	1.90	0.0
15	03/07/2008	7.1	0.020	0.00	0.41	0.00	1.20	0.0
16	04/07/2008	6.8	0.012	0.00	0.39	0.00	1.10	0.0
17	05/07/2008	6.5	0.017	0.04	0.49	0.96	0.20	0.1
18	06/07/2008	6.9	0.008	0.09	0.49	0.00	0.00	0.2
19	07/07/2008	7.2	0.020	0.04	0.51	0.00	0.95	0.1
20	09/07/2008	7.7	0.040	0.13	0.51	0.00	0.31	0.3
21	10/07/2008	7.8	0.027	0.09	0.49	0.00	1.10	0.2
22	11/07/2008	7.3	0.007	0.04	0.46	0.00	0.47	0.1
23	12/07/2008	7.4	0.005	0.00	0.49	0.00	0.79	0.0
24	14/07/2008	7.4	0.007	0.09	0.46	0.00	0.47	0.3
25	15/07/2008	7.0	0.003	0.09	0.51	0.00	0.31	0.3
26	16/07/2008	7.0	0.003	0.09	0.51	0.00	0.47	0.3
27	17/07/2008	7.4	0.003	0.00	0.49	0.00	0.79	0.0
28	18/07/2008	7.4	0.004	0.09	0.51	0.00	0.31	0.3
29	19/07/2008	7.0	0.004	0.04	0.51	0.00	0.95	0.1
30	21/07/2008	7.6	0.005	0.57	0.49	0.00	0.79	1.5
31	22/07/2008	6.9	0.004	0.04	0.49	0.00	0.79	0.1
32	23/07/2008	6.6	0.007	0.00	0.51	0.00	0.31	0.0
33	24/07/2008	7.1	0.032	0.13	0.51	0.00	0.79	0.3
34	25/07/2008	7.5	0.040	0.04	0.44	0.00	0.47	0.1
35	26/07/2008	6.8	0.012	0.00	0.41	0.00	0.31	0.0
36	29/07/2008	6.8	0.009	0.09	0.44	0.00	0.63	0.3
37	30/07/2008	7.2	0.014	0.00	0.46	0.64	0.20	0.0
38	06/08/2008	6.7	0.018	0.00	0.39	0.00	0.79	0.0
39	07/08/2008	6.7	0.015	0.00	0.46	0.00	0.47	0.0
40	08/08/2008	7.2	0.004	0.04	0.51	0.00	1.40	0.1
41	09/08/2008	7.1	0.005	0.09	0.51	0.00	0.79	0.3
42	11/08/2008	7.1	0.006	0.09	0.49	0.00	0.00	0.3
43	12/08/2008	7.1	0.018	0.00	0.15	0.00	0.00	0.0
44	13/08/2008	7.0	0.051	0.44	0.10	5.80	2.70	1.4
45	14/08/2008	7.1	0.020	0.00	0.46	0.32	0.27	0.0
46	15/08/2008	6.9	0.022	0.00	0.44	5.20	2.50	0.0
47	16/08/2008	6.7	0.070	1.35	0.41	0.00	0.95	3.5
48	18/08/2008	7.1	0.025	0.00	0.44	0.00	0.63	0.0
49	19/08/2008	6.6	0.018	0.04	0.39	0.00	0.00	0.1
50	20/08/2008	6.8	0.016	0.00	0.41	0.00	0.63	0.0
51	21/08/2008	6.9	0.033	0.00	0.28	0.32	0.27	0.0
52	24/08/2008	6.7	0.062	0.00	0.26	0.00	0.63	0.0
53	28/08/2008	7.0	0.031	0.04	0.26	0.00	0.48	0.1
54	05/09/2008	7.0	0.031	0.00	0.21	0.00	0.95	0.0
55	07/09/2008	6.9	0.064	0.17	0.44	0.00	0.31	0.3
56	10/09/2008	7.0	0.055	0.09	0.41	0.00	0.31	0.3
57	19/09/2008	7.1	0.019	0.04	0.36	0.00	0.31	0.1
Range		6.5-8.2	0.00-0.16	0.0-1.35	0.08-0.51	0.0- 5.8	0.03- 2.7	0.0-3.5
Mean		7.13	0.03	0.79	0.41	0.23	0.78	0.21
Stand. Deviation		0.33	0.04	0.196	0.12	1.10	0.59	0.52
C.V		4.70	115	24.53	29.26	47.83	75.67	24.78

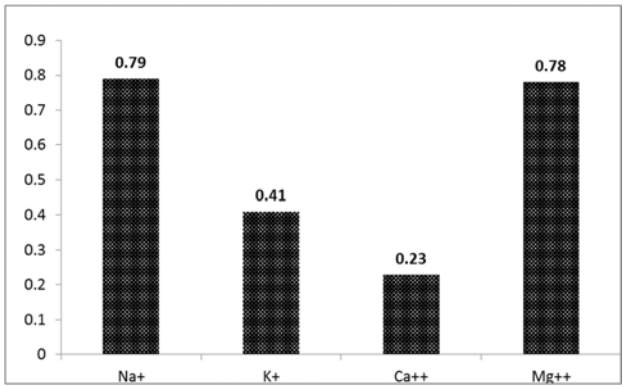

Fig 1: Graphical Presentation of Average Cations Composition in Rainwater of Varanasi ($meqL^{-1}$)

Conclusion

In this investigation the chemical composition of rainwater of Varanasi we have been able to establish a database on the quality of rainwater around one of the high road traffic dens populous city of India. The study revealed that rainwater of the study area is alkaline in nature. pH ranged between 6.5 - 8.2 during the study period, due to the dominance of soil-derived particles. The order of basic cations (mean) found in rain water of Varanasi was as follows: $Na^{+}>Mg^{2+}>K^{+}>Ca^{2+}$ with mean value 2.42 meq L^{-1}.

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