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Potential contamination of basic and acidic anions in rainwater of urban environment: A case study of Varanasi District, Utter Pradesh, India

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Abstract
This study aimed to determine the amount and composition of anions fall with rainwater in urban areas in Varanasi during the south-west monsoon seasons has been studied. The collected rainwater samples have been analyzed for major anions [Cl^-, SO_4^-, CO_3^-, HCO_3 and SO_4^-], pH along with conductivity. The volume weighted pH of rainwater varied from 6.5 to 8.2 with a mean value of 7.1 which is neutral in nature. The range of anions composition in rainwater as follows: 0.20 to 0.70 $meqL^{-1}$ of Cl^-, 0.010 to 1.9 $meqL^{-1}$ of SO_4 -, 0.2 to 1.3 $meqL^{-1}$ of CO_3^-, and 0.0 to 18 $meqL^{-1}$ of CO3 2-, The overall order of anion content in rain water was observed as follows: $HCO_3^- > CO_3 >$ Cl $> SO_4^{2-}$ thus, Basic anions content (CO_3^{2-} and HCO_3^-) in rainwater of Varanasi was much higher than acidic anions content (Cl^- and SO_4^{2-}). About 35% of rainwater samples were observed to be acidic due to high SO_2. Ion. Major part of sulphate ion in rainwater was of anthropogenic origin, i.e. by the oxidation of sulphur dioxide emitted from burning of fossil fuels from Motor vehicles and industries.

Keywords: composition of rainwater, cations contamination, chemistry of rainwater

Introduction

The chemical composition of wet deposition reflects various interacting physical and chemical mechanisms in the atmosphere, which include emission and source amplitude, atmospheric transport processes, atmospheric chemical reactions and removal processes (Galy-Lacaux *et al*., 2009) [1]. Precipitation chemistry also provides a general picture of changes in the composition of the atmosphere caused by anthropogenic activities, as well as changes in meteorology and climate (Vet *et al*., 2014) [2]. The importance of the chemical composition of wet deposition as a source of nutrients, e.g. nitrogen (N), sulphur (S), carbon (C) and base metals, is widely recognised (Duce *et al*., 2009) [3], while precipitation could also be a source of toxic species. Although it can be a very difficult task, it is important to establish atmospheric budgets of key chemical compounds to understand the functioning of ecosystems and biogeochemical cycles (Dentener *et al*., 2006; Davidson *et al*., 2012) [4-5]. Several studies in precipitation chemistry have been done in recent years because of awareness of the impact on the ecosystem by acid rain particularly on human health[6]. Rainwater chemistry also enables to understand the relative importance of different sources of gaseous and particulate pollutants, which have been the subject of immense research in Europe, USA and other parts of the world for the last 30 years [6-11]. Rainwater chemistry in urban areas is attributed to the local pollution sources, whereas in remote and rural areas, it provides the extent of impact of anthropogenic and natural sources. Studies in urban and rural regions in India [12-18] pointed out both man-made and natural pollutants (dust particles) with significant base cations influencing the rainwater chemistry. The acidity of rainwater is completely neutralized by cations prior to its fall on the ground surface. Considering the importance of chemical transformations in polluted atmosphere as well as in precipitation. 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] [19-23]. 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. 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) [24-25]. Quantification of these changes and their effect on terrestrial and aquatic ecosystems is important because of their potential adverse effects (Nriagu and Davidson, 1986) [26]. 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) [27]. Determination of rainwater composition reveals the relative importance of the different sources/types of gases and particulate matter present in the atmosphere. Monitoring the chemical nature of rainwater in Ghana is even more important due to the rapid growth in industrialization, intensive chemical usage in manufacturing processes, oil and mineral exploration and mining. Despite the possible environmental consequences of wet deposition, (Hameed *et al.*, 2004) [28]. is no report concerning the chemical composition of rainwater in Ghana.

Material and Methods

Description Experimental Site and Climatology

Varanasi city (25.28_N; 82.95_E), located in the middle of Ganges valley in North India, is at the Eastern part of Uttar Pradesh, along the left crescent-shaped bank of the Ganges River. The soil surrounding the city is very fertile because low-level floods in the Ganges continually replenish the soil. The city is mostly covered by residential area with heavy road traffic due to unplanned city with small-scale industries. Air quality of Varanasi is very poor due to emissions from badly maintained automobiles and many heavy-loaded transport vehicles. Furthermore, small industries, domestic heating and large-scale constructions contribute to Varanasi's air pollution (Pandey *et al*. 1992) [28]. Moreover, Varanasi faces many problems due to unstable power supply. Most of the businessmen use generator sets for power supply to their shops during power failure, which were operated by kerosene or diesel oil, causing even more environmental burdens to the city. Varanasi experiences a humid subtropical climate with large variations between summer and winter temperatures. Summers are long from early April to October with intervening monsoon (June to September) and are also extremely hot during summer. The temperature ranges between 22 and 46 ^{0}C in the summers. Large diurnal variations during winter with warm days and downright cold nights were seen. Cold waves from the Himalayan region cause temperatures to dip across the city in the winter from December to February, and temperatures below 5^{0}C are not uncommon. The average annual rainfall over this region is1100 mm. Fog is common during winters, while hot dry winds, called heat waves, blow in the summers.

Method and Collection of Rainwater Sample

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 2500 ml). Between two rainfall events the collectors were rinsed by distilled water.

In Banaras Hindu University, the sample collector was placed about 35 meter above the ground level on the roof of Bal Gangadhar Tilak Hostel building during the peak of the raining season May to September in 2009 in 19 cm diameter borosilicate glass funnel tightly fitted to a 5L borosilicate glass bottle that remained outdoors to facilitate collection. The bottles as well as funnels in the collector were cleaned by triple distilled water twice daily in the morning and evening to avoid dry deposition of gaseous and particulate species. Collected samples were kept in pre-washed high-density polyethylene bottles treated with chloroform to minimize microbial activities and were stored in refrigerator at about 4ºC. Other sample used for the determination of trace metal and major cations was kept in an acid-washed bottle. These bottles were soaked in 20% HNO_3 for 24 h, rinsed several times with deionized water and dried before use. Samples collected in acid-washed bottles were acidified with 1ml of 5% ultra-pure HNO_3 to prevent adsorption of the trace metals. All the samples were kept in well-labeled sealed containers and refrigerated until analysis. A total number of 15 rain events were sampled, and a total of 45 samples of rainwater were collected during the monitoring period.

Electrochemical Characterization of Rainwater

A pH meter (Fisherbrand Hydrus 100 model) equipped with glass electrode was used for pH measurement. The pH meter was calibrated using standard buffer solutions of pH 4.01, 7.00, and 9.20 before each measurement. The EC measurements were made using a digital conductivity meter (Hi 9032 Microprocessor model). The instrument was calibrated before the measurements were started.

Analysis of Chloride in Rainwater

The method is based on the titration of a neutral chloride solution with neutral silver nitrate solution in the presence of potassium chromate (K_2CrO_4) indicator. 25 ml aliquot of Rain water sample was taken into a conical flask and 8-10 drops of K_2CrO_4 indicator was added into it. The sample was then titrated against standard 0.05 N $AgNO_3$ from the burette. At the end point, the colour of suspension changed from yellow (due to the presence of $CrO_4{}^{2-}$ ions) to reddish brown (due to the precipitation of red insoluble Ag_2CrO_4).

Method of Analysis of Sulphate in Rainwater

Sulphur was determined turbid metrically as barium sulphate by method of Missouri and Cornfield (1963). 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 $BaCl_2$ crystal were added into it and shaken well. After volume make up, turbidity of the solution was measured in spectrophotometer at 440nm using blue filter. Concentrations of samples were measured from standard curves (K_2SO_4).

Analysis of Carbonate and Bi Carbonate in Rainwater:

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 colour 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 colour 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.

Result and Discussion

Volume weighted mean (VWM), minimum, maximum and standard deviation of major ions along with *p*H and conductivity of rainwater samples collected during summer monsoon season are presented in Table 1. The volume weighted mean *p*H of rainwater was 7.1 which is slightly neutral in nature and varied from 6.5 to 8.2. Figure 1 illustrates the frequency distribution of *p*H with 6.0 -6.5-7.5 30 highest frequency of 35% in the *p*H range 6.5-7.5. These relatively higher values of *p*H in rainwater suggested the dominance of basic components. However, 63% of rainwater was alkaline due to dominance of basic components particularly the presence of carbonates and bicarbonates of calcium. The eastern parts of India are influenced by natural dust particles blown by winds from the nearby arid desert region. University The high specific conductivity (0.335 meq-^{1}) has been found by the dissolution of soil dust also. Kulshrestha *et al.* [10] reported alkaline nature of rainwater in eastern parts of India (Delhi) due to heavy loading of particulate matter rich in carbonate and bicarbonates of calcium, which neutralize the acidity. The values of anionic composition viz. Chloride, sulphate, carbonate and bicarbonate are given in Table 1 and graphical presentation of ions composition viz. Acidic (Chloride &Sulphate) and basic (Carbonate & Bicarbonate) are given in figure 1 and Figure 2 respectively. It was revealed from the data that acidic anions viz. chloride, and sulphate- were found in all the rain water samples in each locations, where basic anions $CO3^{2-}$ was observed in data Table 1 that basic anions content (CO_3^{2-} and HCO_3^-) in rain water of Varanasi was much higher than acidic anions content (Cl^- + SO_4^{2-}) The range of anions in rain water in Varanasi areas as follows: 0.20 to 0.70 meqL-^{1} of Cl^-, 0.010 to 1.9 meqL-^{1} of SO_4 -, 0.2 to 1.3 meqL-^{1} of CO_3^-, and 0.0 to 18 meqL-^{1} of CO3 2-, The overall order of anion content in rain water was observed as follows: HCO_3^- > CO_3> Cl >SO_4 2$^-$ Thus, basic anions in rain water of Varanasi were dominated over acidic anions. The same trend of acidic anions and basic anions were also reported by Khemani *et al.* (1984) [29] in case of rain water of Delhi and Roorkee by Hameed (2001).

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

S. No.	Sampling Date	pH	EC dSm-^{1}	Cl^-	SO_4^{-}	CO_3^-	HCO_3
1	14/06/2008	7.3	0.011	0.3	0.00	0.5	0.0
2	15/06/2008	7.6	0.010	0.4	0.01	0.4	0.0
3	16/06/2008	7.6	0.011	0.3	0.01	0.6	18
4	18/06/2008	7.2	0.033	0.6	0.01	0.5	0.0
5	19/06/2008	8.2	0.150	0.4	0.01	0.8	12
6	21/06/2008	7.3	0.103	0.4	0.00	0.8	0.0
7	22/06/2008	7.7	0.130	0.3	0.03	0.5	12
8	23/06/2008	7.6	0.128	0.5	0.19	0.8	12
9	24/06/2008	7.1	0.029	0.3	0.04	0.3	0.0
10	28/06/2008	7.3	0.071	0.7	0.04	0.9	12
11	29/06/2008	7.1	0.037	0.4	0.05	0.3	0.0
12	30/06/2008	6.9	0.043	0.4	0.05	0.5	6.0
13	01/07/2008	7.1	0.018	0.3	0.01	0.4	0.0
14	02/07/2008	7.2	0.017	0.3	0.02	1.3	0.0
15	03/07/2008	7.1	0.020	0.3	0.02	0.7	0.0
16	04/07/2008	6.8	0.012	0.2	0.01	0.3	0.0
17	05/07/2008	6.5	0.017	0.4	0.00	0.2	0.0
18	06/07/2008	6.9	0.088	0.3	0.00	0.3	0.0
19	07/07/2008	7.2	0.020	0.5	0.02	0.5	0.0
20	09/07/2008	7.7	0.040	0.2	0.05	0.4	0.0
21	10/07/2008	7.8	0.027	0.3	0.03	0.5	0.0
22	11/07/2008	7.3	0.007	0.2	0.04	0.3	0.0
23	12/07/2008	7.4	0.005	0.3	0.01	0.3	0.0
24	14/07/2008	7.4	0.007	0.3	0.08	0.2	0.0
25	15/07/2008	7.0	0.003	0.2	0.13	0.2	0.0
26	16/07/2008	7.0	0.003	0.2	0.19	0.2	0.0
27	17/07/2008	7.4	0.003	0.2	0.13	0.3	0.0
28	18/07/2008	7.4	0.004	0.3	0.05	0.2	0.0
29	19/07/2008	7.0	0.004	0.2	0.03	0.2	0.0
30	21/07/2008	7.6	0.005	0.3	0.01	0.3	0.0
31	22/07/2008	6.9	0.004	0.2	0.03	0.2	0.0
32	23/07/2008	6.6	0.007	0.3	0.04	0.2	0.0
33	24/07/2008	7.1	0.032	0.3	0.05	0.4	0.0
34	25/07/2008	7.5	0.040	0.3	0.02	0.2	0.0
35	26/07/2008	6.8	0.012	0.2	0.03	0.2	0.0
36	29/07/2008	6.8	0.009	0.3	0.03	0.2	0.0
37	30/07/2008	7.2	0.014	0.3	0.03	0.2	0.0
38	06/08/2008	6.7	0.018	0.3	0.04	0.2	0.0

39	07/08/2008	6.7	0.015	0.3	0.04	0.2	0.0
40	08/08/2008	7.2	0.004	0.2	0.02	0.2	0.0
41	09/08/2008	7.1	0.005	0.3	0.02	0.2	0.0
42	11/08/2008	7.1	0.006	0.3	0.00	0.2	0.0
43	12/08/2008	7.1	0.002	0.4	0.02	0.2	0.0
44	13/08/2008	7.0	0.051	0.4	0.02	0.2	0.0
45	14/08/2008	7.1	0.020	0.4	0.01	0.3	0.0
46	15/08/2008	6.9	0.022	0.3	0.01	0.4	0.0
47	16/08/2008	6.7	0.070	0.6	0.08	0.3	0.0
48	18/08/2008	7.1	0.025	0.4	0.02	0.3	0.0
49	19/08/2008	6.6	0.018	0.3	0.01	0.3	0.0
50	20/08/2008	6.8	0.016	0.3	0.02	0.4	0.0
51	21/08/2008	6.9	0.033	0.4	0.03	0.3	0.0
52	24/08/2008	6.7	0.062	0.3	0.05	0.5	0.0
53	28/08/2008	7.0	0.031	0.2	0.05	0.3	0.0
54	05/09/2008	7.0	0.064	0.03	0.3	0.6	0.0
55	07/09/2008	6.9	0.055	0.03	0.2	0.5	0.0
56	10/09/2008	7.0	0.019	0.05	0.3	0.2	0.0
57	19/09/2008	7.1	0.028	0.03	0.3	0.4	0.0
Range		6.5 -8.2	0.002-0.150	0.002-0.150	00-1.9	0.2-1.3	0.0-18
Mean		7.1	0.335	0.335	0.034	0.380	1.30
±SD.		0.335	0.337	0.337	0.034	0.220	0.39
CV.		4.69	0.337	0.337	10.0	57.90	30.0

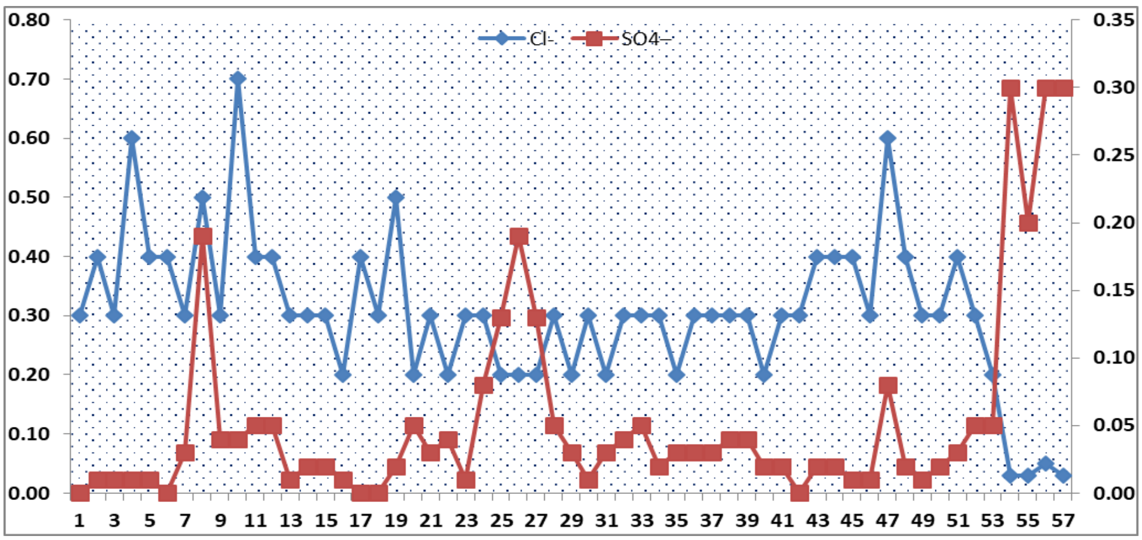

Fig 1: Graphical Presentation of Acidic Anions Composition in Rainwater

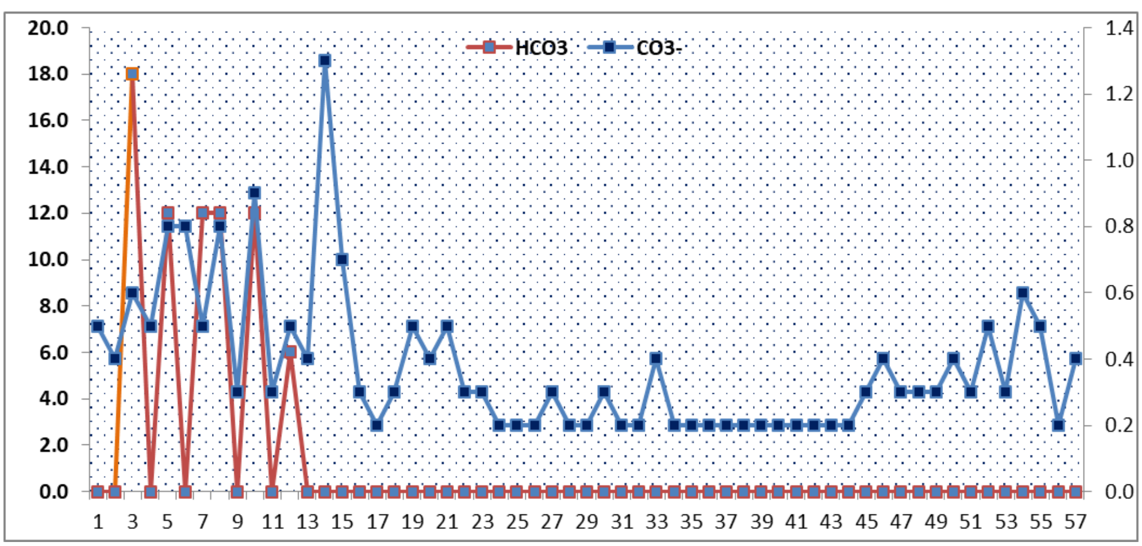

Fig 2: Graphical Presentation of Basic Anions Composition in Rainwater

Conclusions

Chemical composition of rainwater in urban environment of Varanasi of eastern Uttar Pradesh has brought out the following salient features: Bicarbonates and Chloride are the two dominant ions found in rainwater. Role of these ions are important for deciding acidity or alkalinity in rainwater. The average Volume Weighted Mean pH value was found to be 7.1, which shows neutral condition of rainwater. The overall order of anions content in rain water was observed as follows: Bicarbonates> Carbonates>chloride>Sulphate (HCO_3^- > CO_3> Cl >SO_4^{2-}) Thus, basic anions in rain water of Varanasi was dominated over acidic anions.

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