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pH and Chemical Composition of Bulk Precipitation - Karnataka, India

Shivashankara G. P.[1] and Sharmila G.V.[2 +]

[1] Department of Civil Engg., PES college of Engineering, Mandya, Karnataka, India- 571401
[2] Research Scholar, PET Research Centre, PESCE Mandya, Karnataka, India- 571401

Abstract. Precipitation is one of the many manifestations of water in all its forms in the earth atmosphere system. Since precipitation is the primary source of water on land, the formation and spatial variations of precipitation are of much importance for a hydrologist. Bulk (wet+dry) precipitation displays the combined effects of all water soluble components of precipitation. Study on precipitation should be conducted using number of sampling stations, since a single sampling site is biased by its proximity to its pollution source. The main objective of the study is to characterize the bulk precipitation chemistry as influenced by urban, semi-urban and forest areas in the study area. The study includes Hebbal (Mixed), Jayanagar (Residential & commercial) of Bangalore, Mandya (semi-urban) and Ramanagara (Forest) areas. During study period 2009-2011, bulk precipitation samples were collected. Bulk sampler is the common name of a collector that is open all the time. The bulk collector will, apart from the precipitation, also collects direct deposition of aerosols particles and gases like SO_2 and NO_x. The samples collected from the sampling stations were analyzed for pH, cations (Ca^{2+}, Mg^{2+},Na^+, K^+ and NH_4^+-N) and anions (Cl^-, SO_4^{2-}, HCO_3^-, NO_2^--N, NO_3^- -N and PO_4^{3-} -P) as per standard methods (2005). The characterization of bulk precipitation samples shows that the volume weighted mean pH in Hebbal urban area is 4.54, which was acidic in nature, mainly due to local emission of SO_2 and NO_x from industrial and urban activities, and increase in automobiles. Whereas pH of 5.89 (Jayanagar), 6.34 (Ramanagara) and 6.11 (Mandya), which were alkaline in nature, as these regions are influenced by neutralizing ions such as Ca^{2+} and NH_4^+. At Hebbal, the relation between H^+ and SO_4^{2-}yields a positive significant correlation coefficient of 0.8, 0.66 between H^+ and NO_3^-, 0.6 between Ca^{2+} and SO_4^{2-}, 0.63 between $NH_4^+$and SO_4^{2-}. The highly significant positive correlation between H^+ and SO_4^{2-} and NO_3^- leads to the formation of strong acids of H_2SO_4 and HNO_3. The study shows that lower pH in precipitation is controlled by H_2SO_4 and HNO_3 and the sources of SO_4^{2-} and NO_3^- could be emissions from industries and automobiles.

Keywords: Precipitation, pH, Acid rain, Correlation matrix.

1. Introduction

The relative acidity and alkalinity of rainfall is affected by the presence of both acid-producing and alkali-producing constituents in the rainfall. These constituents may be present in the gaseous forms or in particulate forms and may be derived from natural or man-made sources. In the absence of man-made pollutants, raindrops falling through the atmosphere which reach equilibrium with CO_2 which dissolves in water to produce the slightly acidic carbonic acid with an equilibrium pH of 5.6. Precipitation is considered acidic if its pH is less than 5.6. Normal or neutral pH of precipitation is 5.6; it results from the reaction of CO_2 with rain in the atmosphere forming carbonic acid and is assumed to be normal for wet precipitation. Acid rain is caused by the reaction of SO_2 and NO_x with rain water to form H_2SO_4 and/or HNO_3, which freely dissociate and yield hydrogen ions (H^+) and thus lower pH values of precipitation (Cooper et al., 1976). The following represents the formation of carbonic acid (Vermeulen, 1979).

+ Corresponding author. Tel.: +91 9448886809; fax: +91-8232 222075.
E-mail address: gpshivashankara@yahoo.com.

$$CO_2+H_2O \rightleftharpoons HCO_3^- + H^+$$

Generally precipitation, wet precipitation is defined as anything wet fallout from the atmosphere and bulk precipitation is the mixture of rain (wet) and the dry fallout. Bulk precipitation display the combined effects of all water soluble components of precipitation. Dust from the earth's surface is commonly assumed to be alkaline; it is commonly reported in the literature as a constituent of the atmosphere and of precipitation. Alkaline and alkaline earth cations in precipitation are typically attributed to such sources as "soil dust", "terrestrial dust" and "crystal dust". Specific sources include soil, from which wind erosion and filling operations, and also unpaved roads, from which dust is raised by vehicle traffic. Most results indicate that terrestrial sources account for up to 30% of the mass or equivalent of precipitation impurities. The main aim of the present work is to conduct the study on composition of bulk precipitation in urban, semi-urban and forest areas in Karnataka state, India.

2. Methodology

The locations of the sampling stations are shown in Fig.1. For the study purpose, to collect the precipitation samples, the bulk precipitation collectors were placed on the roof of the building. The samples were collected at different sampling stations: Hebbal (Bangalore North), Jayanagar (Bangalore South), Ramanagara and Mandya. The Hebbal is a mixed area i.e., sampling point is surrounded by residential and commercial buildings and large number of industries with very intensive road transport and downwind of Peenya Industrial area. Jayanagar is a residential and commercial area with very intensive road transport. Mandya is a semi urban area and Ramanagara is a forest area, far from intensive road transport.

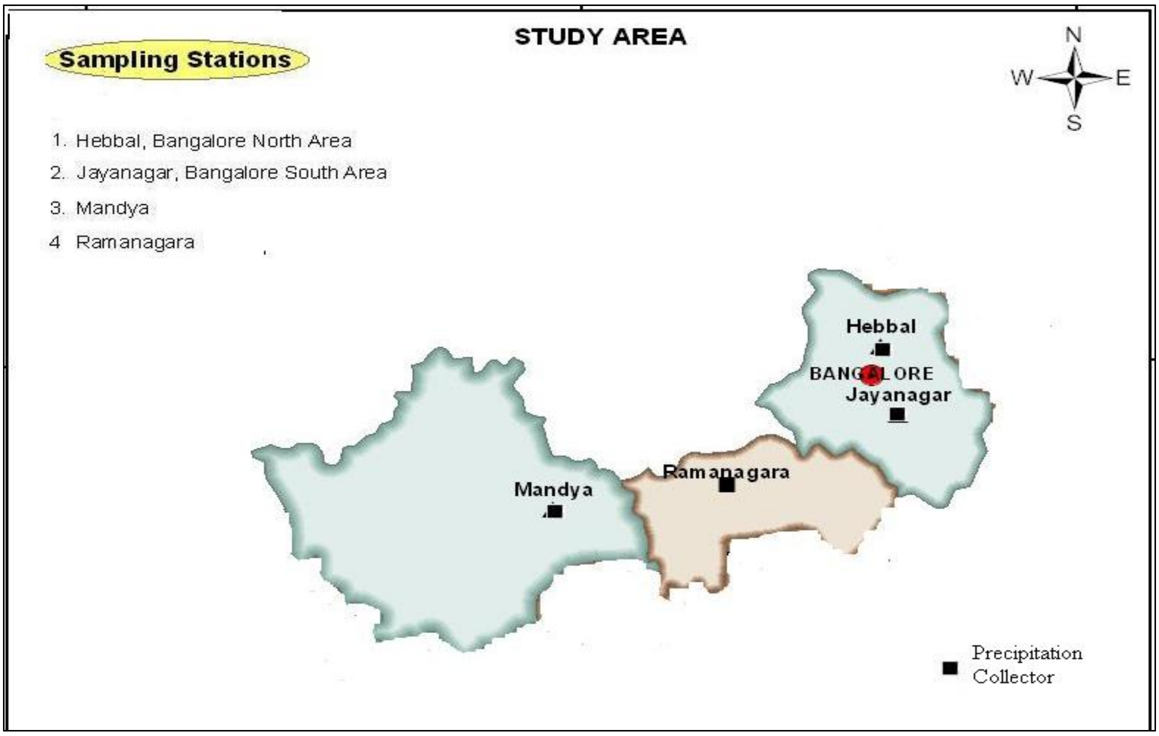

Fig. 1: Location of sampling of precipitation in urban, semi urban and forest area

The bulk precipitation (wet+dry) collector in this study was designed by Likens (1967) and cited by Ramalingaiah (1985) and Shivashankara (1998). The collector consists of a polyethylene funnel (18cm dia) connected to a five liters polyethylene reservoir. The reservoir was attached to a vapor trap, and a vapor barrier using tygon tubing which was provided by a loop to prevent the gas exchange between the atmosphere and the sample and evaporation from the reservoir. A filter was used in the funnel to avoid contamination by insects and litter. Bulk precipitation samples were collected on weekly/biweekly basis from precipitation collector. Every sample included two or more consecutive showers although some samples had one rain event only. During the study period 2009-2011, 206 bulk precipitation samples were collected from all the four sampling stations in the study area. Collected samples were visually inspected for contamination by bird breach and algal growth and such samples were discarded. The samples collected from the sampling stations were analyzed for pH, cations (Ca^{2+}, Mg^{2+},Na^{+}, K^{+} and NH_4^{+}-N) and anions (Cl^{-}, SO_4^{2-}, HCO_3^{-}, NO_2^{-}-N, NO_3^{-} -N and PO_4^{3-} -P) as per standard methods (2005).

3. Results and Discussions

Annual volume weighted average concentrations (VWM) in µeqL^{-1} were calculated for all the chemical constituents of bulk precipitation. The mean VWM of bulk precipitation for all the four sampling stations i.e. Bangalore north (Hebbal), Bangalore south (Jayanagar), Ramanagara and Mandya are presented in Table 1. The study indicates that in the bulk precipitation of Hebbal, SO_4^{2-} is the most abundant anion followed by HCO_3^{-}, NO_3^{-}, Cl^{-}, NO_2^{-} and PO_4^{3-} and Ca^{2+} is the most dominant cation followed by Na^{+}, NH_4^{+}, Mg^{2+}, K^{+}. Also in Ramanagara and Mandya HCO_3^{-} is the dominant anion and $Ca^{2+}$is the dominant cation.

Table 1: Average Volume weighted mean (VWM) of pH and major ions (µeqL-1) of bulk precipitation in sampling stations during 2009-2011.

AREA	pH	H^+	Ca^{2+}	Mg^{2+}	Na^+	K^+	NH_4^+	Cl^-	SO_4^{2-}	HCO_3^-	NO_3^-	NO_2^-	PO_4^{3-}
HEBBAL*	4.54	28.6	108.34	13.65	40.22	12.19	33.57	31.62	117.91	53.72	45.43	5.57	7.16
JAYANAGAR*	5.89	1.29	85.27	8.81	28.07	7.69	28.63	32.02	46.46	41.82	39.12	4.02	6.20
RAMANAGAR	6.34	0.41	84.23	8.31	21.21	4.50	31.82	20.50	24.05	41.90	32.04	1.80	2.84
MANDYA	6.11	0.77	80.84	15.19	32.2	13.40	38.45	31.59	33.69	40.14	37.46	7.29	11.07

* Volume Weighted Mean pH for Bangalore region is 5.22

Review of data from Table 1 shows that, Hebbal of Bangalore VWM pH was 4.54 and Bangalore region is 5.22 which is lower than 5.6. This data indicated that during 2009-2011, VWM was in acidic range. Varma (1989) reported that pH for Bangalore region precipitation had an average of 6.61 for the years 1974-1984. Also Shivashankara et al. (1998) and Munawar Pasha et al. (2010) had reported that, the precipitation over Bangalore city is turning acidic. The data clearly established that the precipitation in Bangalore region showing decreasing trend towards acid precipitation. The probable reasons for decreasing trend can be attributed towards the rapid industrialization, urbanization and also rapid increasing automobiles. The Jayanagar of Bangalore, Mandya and Ramanagara received alkaline precipitation during study period.

3.1. Statistical Correlation Among Alkaline And Acidic Species

Statistical analysis was carried out between ion species in bulk precipitation (Table 2). Correlation indicates the magnitude or the degree of relationship between two related variables, but does not suggest the dependence of one variable on any other. Correlation coefficients among different species are examined to determine the potential sources that influence the precipitation composition and /or the potential origin of some of the species that are transported in the same air masses.

At Hebbal, the relation between H^{+} and SO_4^{2-}yields a positive significant correlation coefficient of 0.8, 0.66 between H^{+} and NO_3^{-}, 0.6 between Ca^{2+} and SO_4^{2-}, 0.63 between $NH_4^{+}$and SO_4^{2-}. The highly significant correlation between H^{+} and SO_4^{2-} and NO_3^{-} leads to the formation of strong acids of H_2SO_4 and HNO_3. The study shows that lower pH in precipitation is controlled by H_2SO_4 and HNO_3 and the sources of SO_4^{2-} and NO_3^{-} could be emissions from industries and automobiles. At Jayanagar, the relation between Ca^{2+} and SO_4^{2-} yields a positive significant correlation coefficient of 0.84, 0.79 between Ca^{2+} and NO_3^{-}. In bulk precipitation, the relation between H^{+} with SO_4^{2-} and NO_3^{-} yielded a positive correlation, but not a significant one, and it may be partial neutralization. At Mandya, the relation between Ca^{2+} and SO_4^{2-} yields a positive significant correlation coefficient of 0.84, 0.55 between Ca^{2+} and NO_3^{-}. In bulk precipitation, the relation between H^{+} with SO_4^{2-} yielded a positive correlation, but not a significant one, and may be partial neutralization. At Ramanagara, the relation between Ca^{2+} and SO_4^{2-} yields a positive significant correlation coefficient of 0.42. Higher values of coefficients between Ca^{2+} with SO_4^{2-}were observed in all area in bulk precipitation, which indicates that the formation of $CaSO_4$ was responsible for completely neutralizing acidity. Based on correlation result,

$(NH_4)_2SO_4$ appears to be universally true has evident from correlation between $NH_4^+$and SO_4^2 in urban, semi-urban and forest area of precipitation.

Table 2: Correlation coefficient of bulk precipitation in the study area during 2009-2011.

STATION	HEBBAL		JAYANAGAR		MANDYA		RAMANAGARA	
Anions / Cations	SO_4^{2-}	NO_3^-	SO_4^{2-}	NO_3^-	SO_4^{2-}	NO_3^-	SO_4^{2-}	NO_3^-
H^+	0.80**	0.66**	0.20	0.33	0.01	-0.05	0.12	0.24
Ca^{2+}	0.60*	0.66	0.84**	0.79**	0.84**	0.55	0.42**	0.24
Mg^{2+}	0.25	0.52	0.24*	0.08	0.26	0.35*	0.62**	-0.13
NH_4^+	0.63**	0.36	0.70**	0.52	0.74**	0.54	0.29*	0.41

*5% and **1% level- positive significant correlation coefficient.

4. Conclusions

On a chemical equivalent basis, the ionic compositions of major ions were Ca^{2+} and SO_4^{2-}. The possible source of Ca^{2+} ions in urban activities (building construction), particularly of soil-derived particulate matter of bulk precipitation. Higher concentration of cations and anions (except H^+) was observed in bulk precipitation mainly due to dry deposition. At Hebbal, the VWM pH is 4.54 for bulk precipitation, lower than the threshold point for neutrality. The pH was acidic there, while at Jayanagar it is slightly alkaline and at Mandya and Ramanagara, it is totally alkaline. Highly positive significant coefficient of Ca^{2+} with SO_4^{2-} were observed in bulk precipitation indicating that the formation of $CaSO_4$ was responsible for completely neutralizing acidity. Ca^{2+} and NH_4^+ are neutralizing ions and in their absence, the pH of bulk precipitation may reduce faster towards acidic range.

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