



## Chemical Composition of Rainwater at an Urban Area during Southwest Monsoon

P.Venkateshwarlu\*, J Satyanarayana

Analytical Chemistry Division, Indian Institute of Chemical Technology, Tarnaka, Hyderabad, India, 500607.

### Abstract:

At Hyderabad during southwest monsoon season of 2008 determine the chemical composition of rainwater. The mean pH of rain water has been observed to be 6.00 with varied from 5.05-7.57. Out of 38 samples, 21% events were in acidic range and remaining samples were in the alkaline ranges compared to 5.60 which point to the pH value of unpolluted water at equilibrium with atmospheric CO<sub>2</sub>. Chemical characteristics of the rain water ionic species were in the following order: Ca<sup>2+</sup>>SO<sup>4-</sup>>NH<sup>4+</sup>>NO<sup>3-</sup>>Na<sup>+</sup>>Cl<sup>-</sup>>HCO<sup>3-</sup>>F<sup>-</sup>>Mg<sup>+2</sup>>Br<sup>-</sup>>K<sup>+</sup>. The acidity of rainwater samples neutralizing by CaCO<sub>3</sub> and NH<sub>3</sub>. The ratios of different components with respect to seawater ratio conceder Na<sup>+</sup> reference sodium is marine origin. SO<sub>4</sub><sup>2-</sup> and Ca<sup>2+</sup> were shows higher than the recommended sea water ratio indicating the significant influence of non-marine sources at site.

**Keywords:** Rainwater, Alkaline pH, Ion Balance, Neutralization factor, Sea salt ratio

Corresponding author mail id:pabbathireddy@gmail.com

### 1. Introduction:

The atmospheric emissions of some gaseous and aerosols are continuously increasing in atmosphere. The primary anthropogenic polluting emissions gaseous are SO<sub>2</sub>, NO<sub>x</sub> and NH<sub>3</sub>. These pollutants may be dissolved and transported by the rainwater to ground. The dissolved gaseous formed an acids are sulfuric and nitric acid, the rainwater nature become acidic these emissions combustion have produced an environmental acidification of rain<sup>[1,2]</sup>. These have been effects on human beings, animals, water, fish, soils and buildings. These acids partially neutralized with ammonia and aerosols before deposited on the ground. During the past several years the world is seriously affected by the acid rain. The seriously affected areas are mainly in the economically developed regions has been a major in many urban and rural areas of North America and Europe<sup>[3-5]</sup>. In India several studies have generally highlighted the alkaline nature of rainwater due to soil derived particles in the atmosphere and chemical composition of rainwater has been carried out at urban and rural locations.<sup>[6-10]</sup>

The chemical composition of rainwater varies from site to site and region to region due to the influence of that area sources, it is affected with anthropogenic sources. The present report is second effort to study the chemical deposition and rainwater quality in this site. The present study reports

chemical composition of rainwater at Hyderabad is large and fast growing urban area in south India and South central part of India.

### 2. Experimental

#### 2.1. Sampling site:

For this study, Hyderabad is an urban site; it is capital of Andhra Pradesh. It lies 17.22°N 78.26°E about 536m above Sea level. The population of the city is 7 millions. The rainwater samples were collected at roof (Top) of the main building of our Institute i.e. Indian Institute of Chemical Technology (IICT), at a height of around 10-12 meters. Fig(1) shows the sampling site.

#### 2.2. Sample collection

At this site, the rainwater samples were collected using funnel and bottle method, on the roof of our Institute. During monsoon of June-September a total 38 samples were collected.

The bottle and funnel has been cleaned before raining, using deionised water. The rainwater samples were collected in 60ml of polyethylene bottle. The collected samples were stored in refrigerator.

#### 2.3. Quality control method:

Ion balance (sum of anions versus sum of cation) is important parameter and agreement between measured and calculated conductivity. A correlation was observed between sum of anions and sum of cations is 0.69 as shows in Fig 2. All the major ionic components were analyzed and

comparison between measured and calculated conductivity of individual samples as shown in Fig 3, correlation of conductivities is 0.69. From these correlations match it is a good quality data of the chemical analysis.

Fig 1: Sampling site Hyderabad, IICT.

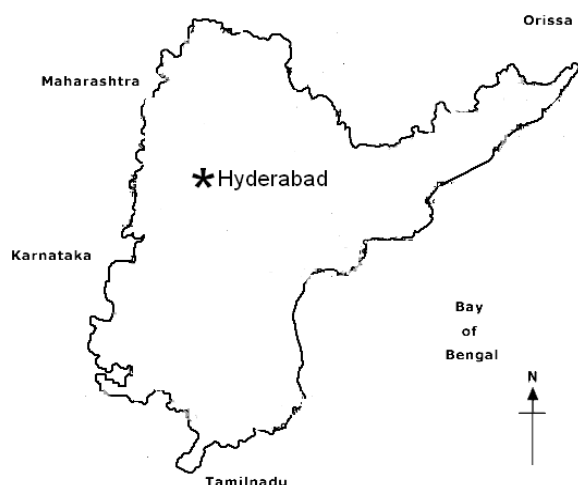


Fig 2: correlation between cation and anions in rainwater.

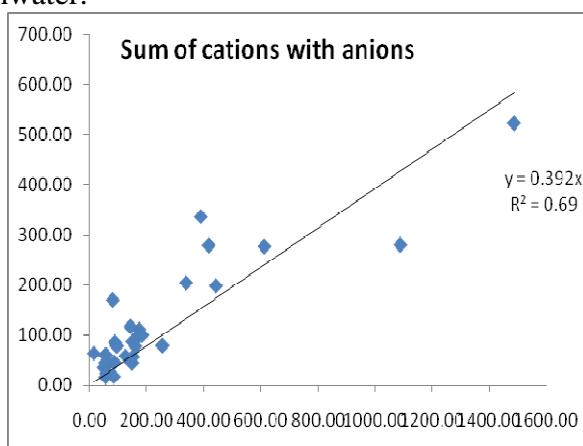
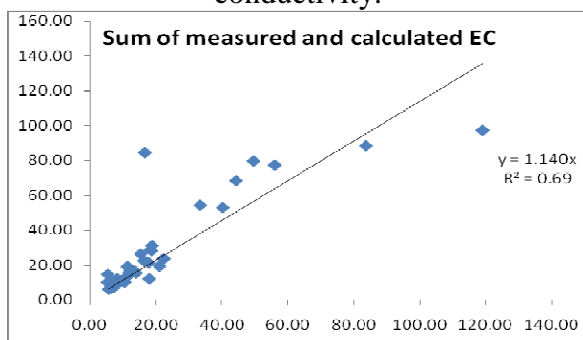


Fig 3: relation between measured and calculated conductivity.



## 2.4. Chemical Analysis:

In the monsoon season collected rainwater samples were brought to laboratory and samples pH and Electrical conductivity (EC) were measured by using pH meter (Elico LI 612), EC was measured by using conductivity meter (Elico CM 183). Anions ( $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ ) and cations ( $\text{Na}^+$ ,  $\text{NH}_4^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ ) were determined by using ion chromatograph (metrohm 792 basic IC system).

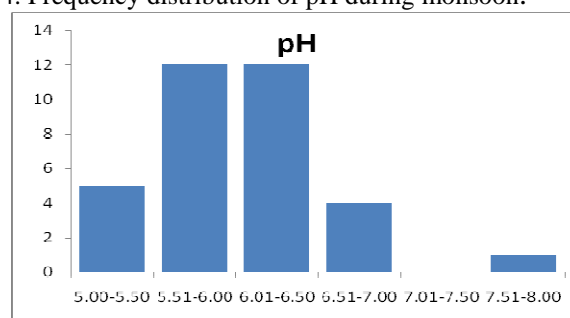
Separation of anions was by metrosep A supp 5-100 column using a mixture of 3.2 mM of  $\text{Na}_2\text{CO}_3$  and 1.0mM  $\text{NaHCO}_3$  as eluent at a flow rate of 0.7ml/min. Cation separation was attempted using a mixture of 4.0mM tartaric acid (TA) and 0.75mM of 2, 6 –pyridine dicarboxylic acid (PDC) as eluent at a flow rate of 1.0ml/min in Metrosep C2-100 column.

## 3. Results and Discussion

### 3.1. Variation of pH:

The pH of 38 samples frequency distributions is plotted in fig-4. In 38 rain samples 79% of the rain event in the alkaline range, as compare to 5.60 which point to the neutral pH value of unpolluted rain water at equilibrium atmospheric  $\text{CO}_2$ . The mean pH of rain water has been observed to be 6.00 with varied from 5.05- 7.57 and. In India pH at urban area is 6.00 to 7.50<sup>[11]</sup> and at rural area is 5.20 to 7.60<sup>[12]</sup>. The high pH of rain water is due to the high loading of particulate matter in the atmosphere in Indian conditions. The suspended particulate matter that is rich in carbonate/bicarbonate of calcium buffers the acidity of rainwater<sup>[7]</sup> during 2008 (June – September) monsoon pH frequency variation shown in Fig 4.

Fig-4. Frequency distribution of pH during monsoon.



### 3.2. Chemical composition:

The ionic species mean concentration has the following order:  $\text{Ca}^{2+} > \text{SO}_4^{2-} > \text{NH}_4^+ > \text{NO}_3^- > \text{Na}^+ > \text{Cl}^- > \text{HCO}_3^- > \text{F}^- > \text{Mg}^{2+} > \text{Br}^- > \text{K}^+$ . The average pH of rainwater alkaline range due to dust particles suspended in the atmosphere. In other Indian site concentration of ionic species are similar Singh *et al.*,<sup>[13]</sup> reported at Rampur, Sastangi *et al.*<sup>[14]</sup>, at Gopalpur. The alkalinity of rainwater in Indian, might be due to soil nature is alkaline. Concentration of  $\text{Ca}^{2+}$  and  $\text{NH}_4^+$ , which are the buffering agents Calcium in the form of Calcium Carbonate and bicarbonate,  $\text{HCO}_3^-$  ion role is impotent in rainwater. No direct method available for measurement of  $\text{HCO}_3^-$ , for estimation  $\text{HCO}_3^-$  theoretical relation between pH and  $\text{HCO}_3^-$  that is  $(\text{HCO}_3^-) = 10^{-11.2+\text{pH}}$ <sup>[7]</sup>. These are the buffering agents in this study. Table 1 shows the average concentration chemical components of rainwater. In rainwater mainly analyzed ions, which are anions ( $\text{Cl}^-$ ,  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ ) and cations ( $\text{Na}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{NH}_4^+$ ),  $\text{NH}_4^+$ ,  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$  are anthropogenic components and  $\text{Ca}^{2+}$  is the earth crust component.  $\text{Na}^+$  and  $\text{Cl}^-$  are the sea salt

fractions those are affected from sea. Acidic pH mainly influences from strong acids in rainwater while neutral or alkaline pH indicates by soil dust and ammonia. Concentrations of these ionic components increased, mainly anthropogenic component concentrations gradually increased and pH decrease, the average of pH was in the alkaline range due to the acidic rainwater neutralized with  $\text{NH}_4^+$  and  $\text{Ca}^{2+}$  soil dust.

### 3.3. Neutralization Factor:

Neutralization factor of  $\text{Ca}^{2+}$ ,  $\text{NH}_4^+$  and  $\text{Mg}^{2+}$  for the four years data, calculated by using of following relation  $\text{NF}(X) = X / (\text{SO}_4^{2-} + \text{NO}_3^-)$ , Where X is  $\text{Ca}^{2+}$ ,  $\text{NH}_4^+$  and  $\text{Mg}^{2+}$  in  $\mu\text{eq/L}$  concentrations. The neutralization factor values of  $\text{Ca}^{2+}$ ,  $\text{NH}_4^+$  and  $\text{Mg}^{2+}$  were 1.86, 1.09 and 0.08 respectively. The present study factors were varied with Indian sites, of Ahmadabad and Pune. Neutralization factor of  $\text{Mg}^{2+}$  only were varied with comparing sites, but lower with given reports. In most of the Indian sites  $\text{Ca}^{2+}$  and  $\text{NH}_4^+$  were major neutralizing components but  $\text{NH}_4^+$  neutralization factor was very high with other Indian sites, may be anthropogenic concentration are high<sup>[15-17]</sup>

Table 1: concentration of ionic species ( $\mu\text{eq/L}$ ) in rainwater.

species	Mean	Median	Minimum	Maximum
$\text{Na}^+$	25.61	13.83	0.00	168.87
$\text{NH}_4^+$	33.58	25.25	0.00	141.17
$\text{K}^+$	2.28	0.00	0.00	15.77
$\text{Ca}^{+2}$	158.63	61.45	10.35	1307.25
$\text{Mg}^{+2}$	4.29	1.71	0.00	29.58
$\text{H}^+$	1.67	1.17	0.03	8.87
$\text{HCO}_3^-$	15.56	5.80	0.71	232.27
$\text{F}^-$	9.08	11.45	0.00	21.26
$\text{Cl}^-$	21.49	14.01	0.28	73.07
$\text{Br}^-$	2.58	1.25	0.00	13.62
$\text{NO}_3^-$	28.67	17.47	2.81	147.06
$\text{SO}_4^{2-}$	38.95	26.32	2.98	131.65

Table 2: Mean Neutralization Factor

Site	$\text{Ca}^{2+}$	$\text{NH}_4^+$	$\text{Mg}^{2+}$	References
Hyderabad	1.86	1.09	0.08	Present study
Ahmadabad	1.77	0.73	0.11	[16]
Pune	1.64	0.66	0.43	[15]

### 3.4. Sea Salt Components:

Table - 3 gives shows the different components of sea salt, non-sea salt and seawater ratio w.r.t  $\text{Na}^+$  reference it is marine origin. At this site,  $\text{Cl}^-$  has been noticed complement of marine origin,  $\text{Cl}^-/\text{Na}^+$  seawater ratio is 1.56 in comparison of standard seawater ratio 1.16. The  $\text{Cl}^-/\text{Na}^+$  indicate the restoration  $\text{Cl}^-$  during the following process. The ratios of  $\text{SO}_4^{2-}$  and  $\text{Ca}^{2+}$  were shows very higher than the recommended sea water ratio, but  $\text{K}^+$  and

$\text{Mg}^{2+}$  these values are similar to the sea water ratio. At present studying site high contribution of anthropogenic and crustal sources of  $\text{SO}_4^{2-}$  and  $\text{Ca}^{2+}$ . Those ionic ratios was high compare to sea water ratio, suggest a non marine origin for these components. Sea salt fraction and non sea salt fraction also calculated, all these ions appear to be a non marine contribution.

Table 3: Comparison of seawater ratios with rainwater components

	$\text{Cl}^-/\text{Na}^+$	$\text{SO}_4^{2-}/\text{Na}^+$	$\text{K}^+/\text{Na}^+$	$\text{Ca}^{2+}/\text{Na}^+$	$\text{Mg}^{2+}/\text{Na}^+$
See water ratio	1.16	0.125	0.227	0.0218	0.439
Ratio in rain water	1.56	4.96	0.11	8.06	0.30
%SSF	100.00	7.42	4.06	0.93	100.00
%NSSF	0.00	92.58	95.94	99.07	0.00

### 3.5. Anthropogenic and crustal Components:

Anthropogenic activity components are  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$  and  $\text{NH}_4^+$ . The nature of rainwater is greatly influenced by these three ionic species, at the site, the concentrations of there ions are observed to be high because of chemical industries and vehicles are growing habitual, continues rain the anthropogenic activities concentrations increase. Crustal components have been described based on  $\text{Ca}^{2+}$  and  $\text{HCO}_3^-$  come from soil dust. In India, soils are alkaline contains high  $\text{CaCO}_3$  during rainy weather conditions; the soil is suspended into the atmosphere which is removed by rain<sup>[7]</sup>. In this site anthropogenic and crustal component concentrations are gradually increase. Due to this reports pollutions were increasing.

### 4. Conclusion:

At Hyderabad during southwest monsoon season of 2008 determine the chemical composition of rainwater. The mean pH of rain water has been observed to be 6.00 with varied from 5.05-7.57. Out of 38samples, 21% events were in acidic range and remaining samples were in the alkaline range as compare to 5.60 which point to the pH value of unpolluted water at equilibrium with atmospheric  $\text{CO}_2$ . Chemical characteristics of Rainwater ionic species were in the following order:  $\text{Ca}^{2+} > \text{SO}_4^{2-} > \text{NH}_4^+ > \text{NO}_3^- > \text{Na}^+ > \text{Cl}^- > \text{HCO}_3^- > \text{F}^- > \text{Mg}^{2+} > \text{Br}^- > \text{K}^+$ . The acidity of rainwater samples neutralizing by  $\text{CaCO}_3$  and  $\text{NH}_3$ . Anthropogenic components concentrations are increasing at urban areas. The ratios of different components w.r.t seawater ratio concenter  $\text{Na}^+$  reference Sodium is marine origin.  $\text{SO}_4^{2-}$  and  $\text{Ca}^{2+}$  were shows higher than the recommended sea water ratio indicating the significant influence of non-marine sources at site.

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