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## ASPECT QUALITATIF DE LA VARIABILITÉ SPATIO-TEMPORELLE DES EAUX

### QUALITY OF RAINWATER OVER VISAKHAPATNAM CITY, INDIA

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**ABSTRACT** About 207 daily bulk rainwater samples from thunderstorms, southwest monsoon and northeast monsoon rains were collected during four year period. The samples were analysed for conductivity, total hardness as  $\text{CaCO}_3$ ,  $\text{Cl}^-$ ,  $\text{HCO}_3^-$ ,  $\text{SO}_4^{2-}$  and  $\text{Ca}^{2+}$ .  $\text{Mg}^{2+}$  and  $\text{Na}^{++} + \text{K}^+$  were estimated. In addition, rainfall was measured with a non recording raingauge at the sampling site. It is observed that southwest monsoon rains show large variations in ionic concentrations when compared with summer and northeast monsoon rains. In general the ionic concentrations are observed to be decreasing from summer rains to northeast monsoon rains. Thunderstorm rains contribute very high sulphate concentrations whereas northeast monsoon rains exhibit very low values. The results are discussed in the paper.

#### INTRODUCTION

In general, the chemistry of rainwater is related to the origin of vapor masses. However, it is usually modified during its circulation over the continent by collecting many air borne particles released from industrial and urban environments. In addition, the dust from the geological formations associated with heavy winds before the rain, particularly in tropical regions, may also contribute to changes in rainwater quality.

For regions adjoining sea, the rainwater deposits considerably on to the land salts derived from marine origin. However, it was observed that several ions inherited from sea water are lost and sometimes replaced by compounds originating from the continent (Junge, 1963). Hydrometeorological phenomena of the region controls the depositional aspects of salts from various sources.

There are not many systematic studies made about the chemistry of rainfall over Southeast Asia as well as India, a region intensely affected by monsoon activity. Handa (1969) has reported some investigations of rainwater chemistry of northern part of India. However, no such detailed studies were reported from southern part of India which is subjected to southwest as well as northeast monsoon activity. The present paper gives some detailed temporal studies of major ion concentrations in rainwater made over Visakhapatnam city located in the southern part of India.

#### STUDY AREA

Visakhapatnam city lies on the east coast of south India adjoining Bay of Bengal and is enclosed between latitudes  $17^\circ 40' \text{N}$  -  $17^\circ 46' \text{N}$  and longitudes  $83^\circ 09' \text{E}$  -  $83^\circ 20' \text{E}$ . It is surrounded by Kailasa hill ranges on the north, Yarada hill ranges on the south, Narava hills on the west and flanked by sea on the eastern side. Due to the strategic situation of the city, there is rapid industrialization and urbanization taking place during the last three decades which may have impact on the precipitation chemistry.

The area has average rainfall of 980 mm per year. Hydrometeorological studies classi-

Table 1. - Range and Arithmetic means for various parameters during different periods.

Parameter	Total rains			Summer			SWmonsoon			NEMONsoon		
	Max.	Min.	Av.	Max.	Min.	Av.	Max.	Min.	Av.	Max.	Min.	Av.
Rainfall(mm)	212.0	0.3	16.6	42.0	2.0	13.9	115.4	0.3	13.0	212.0	0.7	25.5
Conductivity	971.0	6.0	101.0	296.0	9.0	120.3	971.0	15.0	120.1	165.0	6.0	53.3
$\text{Cl}^- (\text{mg l}^{-1})$	154.0	2.5	15.1	100.0	5.0	27.5	154.0	3.0	16.3	80.0	2.5	10.3
$\text{HCO}_3^- (\text{mg l}^{-1})$	305.0	6.1	65.7	219.6	6.1	86.9	305.0	9.8	72.5	195.2	9.8	46.8
$\text{SO}_4^{2-} (\text{mg l}^{-1})$	110.0	0.1	7.8	80.0	2.0	16.9	110.0	traces	9.5	25.0	0.1	2.6
$\text{Ca}^{2+} (\text{mg l}^{-1})$	56.0	0.2	9.4	30.0	0.8	12.4	56.0	0.4	10.4	24.0	0.2	6.5
$\text{Mg}^{2+} (\text{mg l}^{-1})$	41.6	0.1	5.6	26.8	1.9	11.5	41.6	0.1	6.0	22.9	0.5	3.7
$\text{Na}^+ + \text{K}^+ (\text{mg l}^{-1})$	85.8	0.3	16.8	43.4	10.3	22.8	85.8	0.3	18.6	55.3	0.6	11.8
T.H.( $\text{CaCO}_3$ )	225.0	5.0	46.9	180.0	10.0	78.0	225.0	7.0	51.5	100.0	5.0	31.7
Total Anions	389.2	14.8	88.6	251.6	62.9	131.3	398.2	18.2	98.3	203.2	14.8	59.7
Total Cations	131.0	4.2	31.8	567.2	48.0	261.4	131.0	6.1	35.1	66.2	4.2	22.0

fied the region to be varying between semiarid and dry subhumid (Sarma and Swamy, 1984). Most of the rainfall over the city occurs during southwest monsoon (June-Sept.) and northeast monsoon/post monsoon (Oct.-Nov.) in association with bay depressions and storms. The summer rains (April-May) over the city are due to relatively intense convection in humid air causing thunder and lightning. These are called "thunderstorms" usually associated with a violent type of instability shower. The rocks of the region weather to form red loamy lateritic soils on the surface which is the source for the wind blown dust.

**SAMPLE COLLECTION AND ANALYSES**

As a part of routine hydrometeorological investigations 207 daily bulk rainwater samples were collected during summer, southwest monsoon and northeast monsoon periods of the years 1974-1977 at Geophysics Department of Andhra University, Visakhapatnam which is located about 3 km away from the sea. In addition, rainfall was measured with an ordinary 8" non recording raingauge at the site. The rainwater samples were analysed for chemical quality in the laboratory of Geophysics Department within 48 hours. No attempt was made to separate the suspended matter. The samples were tested for their electrical conductivity with the help of Philips Conductivity Bridge No. GH4249. Analyses for  $\text{HCO}_3^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{Cl}^-$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$  and total hardness as  $\text{CaCO}_3$  were conducted using standard methods (Taylor, 1958). The  $\text{Na}^+$  content was estimated as  $\text{Na}^+ + \text{K}^+$  by deducting the sum of  $\text{meq l}^{-1}$  of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  from the sum of  $\text{meq l}^{-1}$  of the anions. Though this is not a valid method for determining  $\text{Na}^+$  ion concentration in rainwater, due to non availability of facilities to analyse  $\text{Na}^+$  and  $\text{K}^+$  individually, the above method was adopted.

**RESULTS**

The composition of salts in rainwater are controlled by the chemical composition of seawater as well as the presence of suspended dust of terrestrial origin in the atmosphere. Loewengart (1964), Yaalon (1962), Dalal (1979), Dethier (1979) and others classify the salts in rainwater and relate ions such as  $\text{Na}^+$ ,  $\text{Mg}^{2+}$  and  $\text{Cl}^-$  to marine origin, and  $\text{HCO}_3^-$ ,  $\text{SO}_4^{2-}$  and  $\text{K}^+$  to terrestrial origin. It was also observed that the distance of sample collection site from the sea inversely influences precipitation of  $\text{Na}^+$  and  $\text{Cl}^-$ . As the sampling site in the present study is only 3 km from the sea, it is expected that sea spray influence should dominate the rainwater quality.

*Ionic concentrations*

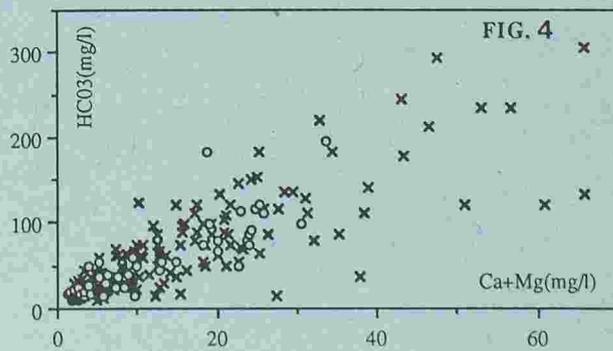
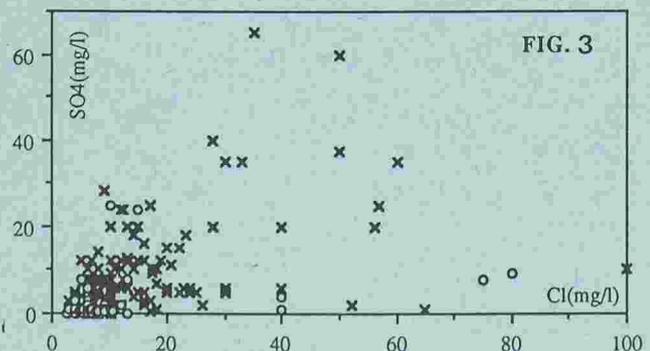
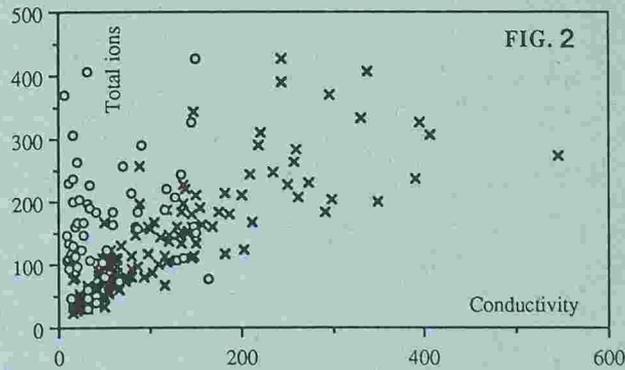
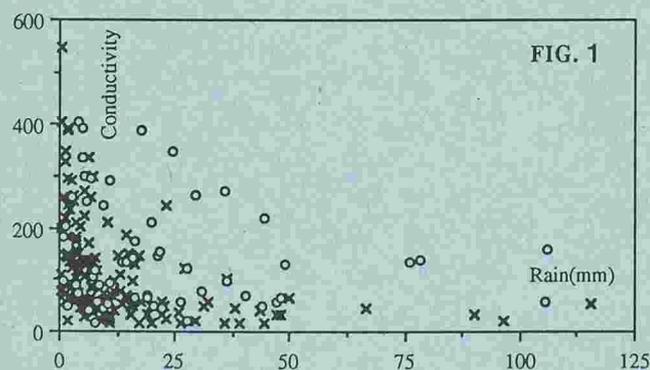
The maximum, minimum and arithmetic mean for various parameters and ions in the rainwater at Visakhapatnam during different seasons of the four year period are given in Table 1. It is observed that on an average various ionic concentrations are highly variable indicating the impact of complicated urban and marine environments of Visakhapatnam region. The difference between maximum and minimum values are particularly high during southwest monsoon period. The maximum concentrations of different ions in various seasons also shows the highest values in southwest monsoon period. Table 1 also indicates that various average ionic concentrations are decreasing from summer months associated with thunderstorm rains to northeast monsoon months associated with cyclonic storms.

In all the samples, the anions are observed to be dominant over the cations. Among the anions  $\text{HCO}_3^-$  is dominant followed by  $\text{Cl}^-$  and  $\text{SO}_4^{2-}$  where as the concentration of  $\text{Na}^+ + \text{K}^+$  is maximum in cations followed by  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ . This indicates the strong influence of terrestrial dust and other pollutants as well as sea spray on rainwater

chemistry of Visakhapatnam. Figure 1 shows the relationship between rainfall and conductivity. There exists an inverse logarithmic relation between these parameters ( $r = -0.4$ ). However, the correlation is not good due to the influence of atmospheric pollution. It is also observed that other solute concentrations are inversely related to the quantity of rainwater with poor correlations. Figure 2 shows the relationship between conductivity and total ionic concentration where southwest monsoon rains show good positive correlation at lower concentration values. The dispersion is more for higher values of the parameters. In general, conductivity gives a good indication of pollution due to various sources. The observed dispersion and high values of conductivity may be due to the effect of pollutants on rainwater. The figure also shows the irregular scatter of the parameters during northeast monsoon rainfall indicating the erratic contribution of cyclonic storms that occur during the period to the rainwater chemistry.

*Analyses of Ratios*

The ratio values of  $\text{Na}^+/\text{Cl}^-$ ,  $\text{Na}^+/\text{Mg}^{2+}$ ,  $\text{Na}^+/\text{Ca}^{2+}$  and  $\text{Cl}^-/\text{SO}_4^{2-}$  in seawater are 0.55, 7.78, 26.25 and 21.47 respectively (Krauskopf, 1967). Table 2 shows the maximum, minimum and mean values of various ratios of major ions in the rainwater at Visakhapatnam during different seasons. Figures 3 and 4 presents the relationships between  $\text{Cl}^- - \text{SO}_4^{2-}$  and  $\text{Ca}^{2+} + \text{Mg}^{2+} - \text{HCO}_3^-$  ions respectively. The linear relationship between  $\text{HCO}_3^-$  and  $\text{Ca}^{2+} + \text{Mg}^{2+}$  (fig. 4) shows that on an average these ions originate from the same source. Among the 207 rainwater samples analysed, 175 exceed  $\text{Na}^+/\text{Cl}^-$  ratio of seawater indicating the dominance of origin of these ions from sea spray. However, all the ratio values of  $\text{Na}^+ + \text{K}^+/\text{Ca}^{2+}$  are less than seawater ratio, thus indicating the origin of  $\text{Ca}^{2+}$  ion from continental sources. In fact,  $\text{HCO}_3^-$  and  $\text{Ca}^{2+}$  pri-



x : SW monsoon o : NE monsoon

Table 2. — Range and arithmetic means for various ratios during different periods (ionic concentrations in mg l<sup>-1</sup>).

Ratio	Total rains			summer			southwest monsoon			northeast monsoon		
	max.	min.	av.	max.	min.	av.	max	min.	av.	max.	min.	av.
Cl <sup>-</sup> /HCO <sub>3</sub> <sup>-</sup>	16.393	0.031	0.455	16.393	0.059	2.267	2.075	0.035	0.310	7.653	0.031	0.554
Ca <sup>2+</sup> /Mg <sup>2+</sup>	80.000	0.038	3.303	2.483	0.127	1.042	80.000	0.038	3.536	12.941	0.092	2.295
Na <sup>+</sup> + K <sup>+</sup> /Cl <sup>-</sup>	6.458	0.040	1.471	3.500	0.407	1.424	4.886	0.040	1.467	6.458	0.046	1.488
Na <sup>+</sup> +K <sup>+</sup> /Ca <sup>2+</sup>	8.800	0.006	0.665	4.375	0.014	0.752	5.687	0.006	0.488	8.800	0.009	1.065
Cl <sup>-</sup> /SO <sub>4</sub> <sup>2+</sup>	130.000	0.321	9.550	5.600	1.000	2.326	100.000	0.321	8.140	130.000	0.400	13.876
Na <sup>+</sup> +K <sup>+</sup> /Mg <sup>2+</sup>	210.000	0.088	6.720	11.053	0.716	3.271	210.000	0.088	7.500	26.333	0.316	5.347

marily result of reactions between atmospheric CO<sub>2</sub> and Ca compounds present as dust. Na<sup>+</sup> + K<sup>+</sup>/Mg<sup>2+</sup> ratio (Table 2) indicates very wide range of variation. The average values are nearer to seawater ratio, thus indicating the marine origin of Mg<sup>2+</sup> ion. The percentage of SO<sub>4</sub><sup>2-</sup> of marine and continental origin dissolved in rainwater of Visakhapatnam is computed using the ratio (Miwutani and Rafter, 1969) as:

$$(Cl^- (mg l^{-1}) / 7.1 SO_4^{2-} (mg l^{-1})) \times 100$$

It is observed that the sulphate of 76% of rainwater samples is of marine origin and the remaining 24% is of terrestrial origin. The SO<sub>4</sub><sup>2-</sup> content of thunderstorm rains during summer may be explained by entrainment of S of terrestrial origin by raindrops during their downward passage (Nakai and Jensen, 1967; Cortecci and Longinelli, 1970). In addition, very low concentrations of SO<sub>4</sub><sup>2-</sup> ion were observed

from the cyclonic precipitation associated with northeast monsoon rainfall which derives moisture from sea.

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