Spatial Variations of Groundwater Vulnerability using Cluster Analysis

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Abstract: An investigation on quality of groundwater has been carried out in the river basin of Varaha located in Visakhapatnam District, Andhra Pradesh to find out the factors that are responsible for spatial variations of water vulnerability. The study area is underlain by the Precambrian rocks of Eastern Ghats over which the Recent Formations occur. Groundwater is a prime source for drinking and irrigation. The quality of groundwater is fresh and brackish with dominance of the latter. Groundwater samples are categorized into two major clusters A and B, using the dendrogram of cluster analyses. Out of these two major clusters, five sub-clusters I to V in the pre-monsoon season and six sub-clusters I to VI in the post-monsoon season are identified. The sub-clusters I to IV of pre-monsoon and I to V of post-monsoon seasons of the cluster A are characterized by less mineralized groundwater compared to those of V of pre-monsoon and VI of post-monsoon seasons of the cluster B, which represent highly mineralized groundwater. The low to high mineral content follows gradually from upstream to the downstream area, being higher in post-monsoon season in both the clusters A and B, depending upon the source, mineral dissolution, and precipitation, solubility and leaching of ions, ion exchange and adsorption processes. Spatial distributions of the sub-clusters give clues to understand the factors that cause variations of groundwater vulnerability at a specific site, vis-a-vis local and regional lithological and non-lithological influences. As a result, the quality of groundwater on a regional scale changes from $Na^+ > Mg^{2+} > Ca^{2+} > K^+$: HCO₃ > Cl⁻ $> SO_4^{2-} > NO_3^- > F^-$ in the cluster A to $Na^+ > Mg^{2+} > Ca^{2+} > K^+$: Cl⁻ $> HCO_3^- > SO_4^{2-} > NO_3^- > F^-$ in the cluster B, following the topography. The classification of the area into the zones of relative groundwater vulnerability with respect to drinking water quality of the chemical composition of the sub-clusters helps the planners to identify the specific locations, where the inferior quality of groundwater can occur, for taking the remedial measures.

Keywords: Cluster analysis, Spatial variations, Groundwater vulnerability zones, Groundwater quality, Andhra Pradesh.

INTRODUCTION

Groundwater is a natural replenishable resource. It becomes an important source for any developmental activities due to shortage of surface water and frequent failures of monsoon. Increasing demand for groundwater causes decline in water levels as well as deterioration in water quality. In general, water without potable quality cannot be useful for any purpose. On the other hand, the assessment of spatial variations of groundwater vulnerability is a big problem due to involvement of so many factors like distribution of rainfall, run-off, grain size of soil, topographic features, type of landforms, drainage conditions, lithological characteristics, land use practice, depth to groundwater and environmental constraints, which are not uniform in any area.

Though the interpretation of groundwater chemistry is frequently done, with the help of graphical displays, such as Piper's, Schoeller's and Durov's diagrams (Piper, 1944; Schoeller, 1962; Zaporozec, 1972), they do not explain satisfactorily the factors which cause variations in groundwater quality on a regional scale (Dalton and Upchurch, 1978; Melloul and Collin, 1992; Guler et al. 2002; Mahlknecht et al. 2004). Thus, the aim of the present paper is to find out the factors that are responsible for variations in groundwater vulnerability at a specific site, using cluster analysis.

STUDY AREA

Location

The study area drained by the river Varaha, lying between latitudes $17^{\circ}23'$ and $17^{\circ}55'$ N and longitudes $82^{\circ}30'$ and 82°53' E, is located in Visakhapatnam district, Andhra Pradesh (Fig.1). The climate is dry, with mean annual temperatures of 20°C to 36°C. The mean annual rainfall is 1,200 mm. The river Varaha originates from the Eastern

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Fig.1. Location of the study area.

Ghats at an altitude of about 1,165 m above mean sea level (amsl), flows 62 km towards the southeast and finally joins the Bay of Bengal. The drainage is mostly dendritic and is ephemeral in character.

Geology

The study area is characterized by undulating topography sloping towards the southeast. It is underlain by Precambrian rocks and Recent formations (Fig. 2). The Precambrian rocks include khondalites and charnockites, with intrusive bodies of quartz, pegmatite, migmatite and granite. The former are the most dominant, containing quartz, plagioclase and orthoclase feldspars, garnet and sillimanite as essential minerals; and apatite, biotite and opaques as accessories. The latter occur as isolated patches that are composed of quartz, potash and plagioclase feldspars, ortho- and clinopyroxenes, with garnet as essential minerals; and biotite, apatite, zircon and opaques as accessory minerals. The foliation trend of the khondalites is towards NE-SW, with a deviation of NNW-SSE, N-S and NNE-SSW, and a dip of 70° southeast. The Recent formations overlie the Precambrians. They include the sediments of silt loams, loamy sands, colluvium, coastal sands and marine clays. Red soil is the dominant type. The concentrations of $CaCO₃$, locally known as *kankar*, occur as intercalations in the soil zone.

Hydrogeology

Groundwater is the main source for drinking and irrigation due to lack of surface water as a result of erratic rainfall. It occurs in the weathered and fractured portions of the Precambrian rocks as well as in the Recent sediments. Depth of water level varies from 3 to 15 m below ground level between pre- and post-monsoon seasons, being shallow in the latter.

Land use/Land cover

About 65% of the total study area is occupied by the agricultural land, 21% by the waste land, 8% by the forest land, 5% by the built-up land, and the remaining 1% of the land is covered by the water bodies. Irrigation is intensive. Unlimited usage of fertilizers for higher crop yield and addition of gypsum for soil improvement are not uncommon practices in the area. Dumping of domestic wastes in the empty places, seepage of sewage waters and leakage of septic tanks are common sources of pollution.

METHODOLOGY

Sampling, Cluster Analysis and Analytical Procedures

Thirty groundwater samples were collected in 500 ml

Fig.2. Geology of the study area.

polyethylene bottles from dug wells in the study area (Fig. 1) during pre- and post-monsoon of 2008. The samples were classified into two major clusters A and B, and five sub-clusters I to V in the pre-monsoon season and six sub-clusters I to VI in the post-monsoon season (Figs. 3 and 4), following the STATISTICA version 6.1. Hierarchical cluster analysis adopted here is a powerful grouping mechanism to classify the samples genetically, so that the samples of the resulting clusters are similar to each other, but distinct from the other clusters. In this analysis, a complete linkage is used to determine the distance between the clusters by the greatest distance between any two

objects in the different clusters. The euclidean distance is selected between the samples, as it is a geometric distance in a multidimensional space.

A graphical representation of the hierarchical clustering along with the corresponding distance to achieve a linkage is called a dendrogram (Figs. 3 and 4). The clusters identified from the hierarchical cluster analysis are used for a more comprehensive interpretation of the chemical data in terms of 10 variables (pH, Ca^{2+} , Mg^{2+} , Na^{+} , K^{+} , HCO_3^- , Cl^- , SO_4^{2-} , NO₃ and F⁻), computed from the analysis of groundwater samples, following the standard water quality procedures of APHA (1992). Summary of the methods used for the chemical analysis of groundwater is presented in Table 1.

Ionic-balance-error

The chemical data of groundwater samples are subjected to compute the ionic-balance-error between the Total Concentration of Cations $(Ca^{2+}, Mg^{2+}, Na^{+}$ and K+) and Total Concentration of Anions (HCO₃, Cl⁻, SO₄², NO₃ and F– ; Eq. 1) for testing accuracy of chemical analysis of each groundwater sample, before the interpretation of the chemical data is undertaken. The value of the ionic-balance-error is observed to be within the acceptable limit of ±5% (Domenico and Schwartz, 1990).

Ionic-balance-error =
$$
\left[\frac{(TCC - TCA)}{(TCC + TCA)}\right] \times 100 \quad (1)
$$

Saturation Index

To predict the mineral state, whether it is in dissolved state (undersaturation), or in equilibrium state (saturation) or in precipitated state (oversaturation) in groundwater, the saturation index is computed (Eq. 2), following the

Figs.3-4. Hierarchical cluster analysis dendrogram phenon line, which is chosen to select the number of observed clusters. (**3**) Pre-monsoon. (**4**) Post-monsoon.

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Table 1. Methods used for the chemical analysis of groundwater

	Chemical variables	Expressed Method
pН	(units)	pH meter
Ca^{2+}	(mg/l)	Titration with EDTA
Mg^{2+}	(mg/l)	Calculation $(TH-Ca^{2+})$
$Na+$	(mg/l)	Flame photometer
K^+	(mg/l)	Flame photometer
HCO ₂	(mg/l)	Titration with HCl
Cl^-	(mg/l)	Titration with AgNO ₃
SO_4^{2-}	(mg/l)	Spectrophotometer
NO ₂	(mg/l)	Colorimeter
$_{\rm F}$ -	(mg/l)	Spectrophotometer

WATERQ programme.

Saturation index =
$$
\log_{10} \frac{K_{IAP}}{K_{SP}}
$$
 (2)

where K_{IAP} is the ion activity product of particular mineral phase and K_{SP} is the solubility product of that phase.

RESULTS AND DISCUSSION

Groundwater Quality

The pH (units) and the concentrations (mg/l) of Ca^{2+} , Mg^{2+} , Na⁺, K⁺, HCO₃, Cl⁻, SO₄², NO₃ and F⁻ vary from 7.1 to 8.2, 30 to 75, 25 to 115, 159 to 883, 8 to 38, 370 to 970, 130 to 1,470, 21 to 170, 14 to 54 and 0.60 to 2.10, with a mean of about 7.73 to 7.79, 52 to 54, 48 to 57, 306 to 386, 14 to 19, 596 to 654, 308 to 430, 60 to 67, 34 to 36 and 1.15 to 1.28 during the pre- and post-monsoon seasons, respectively, being the higher concentrations in the postmonsoonseason (Table 2).

The concentration levels of Mg^{2+} , Na⁺, Cl⁻, SO₄², NO₃² and F– ions (Table 2) are sometimes higher than the acceptable limits of 30, 200, 250, 150, 45 and 1.20 mg/l prescribed for drinking water, causing a scale formation in well structures, hypertension, salty taste, bitter taste, blue baby syndrome called *methaemoglobinemia* and fluorosis, respectively, (Holden, 1970; BIS, 2003; WHO, 2004).

Origin of Dissolved Ions

Lithology is the main source of cations, such as Ca^{2+} , Mg^{2+} , Na⁺ and K⁺ (Hem, 1991). The weathering of the country rocks and the dissolution of feldspar (plagioclase and potassium varieties) and ferromagnesium minerals (garnet, biotite, sillaminite and pyroxenes) in carbonic acid (H_2CO_3) contribute to the cations (Eq. 3). Besides, the ions Mg^{2+} and Na⁺ also result from the influences of nonlithological sources of anthropogenic (such as dumping of domestic wastes in the empty places, seepage of sewage waste waters, leakage of septic tanks, as well as intensive and long-term irrigation practice (associated with the prolonged irrigation-return-flows and continuous usage of unlimited fertilizers for higher crop yields) and marine clays. Among anions, the ion HCO_3^- is from a lithological source, which is caused by the interaction of $CO₂$ with the water present in the soil zone (Eqs. 4 and 5). The CO_2 also releases into the soil zone due to decay of organic matter and root respiration. On the other hand, the Cl⁻, SO_4^{2-} and NO₃ ions are mainly non-lithological in origin, and are due to soil amendments used for its improvement in the study area. However, the ion Cl⁻ along with the ion Na⁺ are contributed from the clay products due to sluggish drainage conditions (Hem, 1991). The ion F– is derived from both lithological (minerals of apatite, biotite and clay, occurring in the country rocks) and non-lithological (chemical fertilizers) sources.

Cation-silicates (s) + H₂CO₃ (aq)
$$
\Rightarrow
$$
 H₄SiO₄ (aq) + HCO₃ (aq) + Ca²⁺ (aq) + Mg²⁺ (aq) + Na⁺ (aq) + K⁺ (aq) + clays (s)

\n(3)

$$
CO2(g) + H2O (l) \Rightarrow H2CO3(aq)
$$
 (4)

$$
H_2CO_3 \text{ (aq)} \Rightarrow H^+ \text{(aq)} + HCO_3^- \text{(aq)} \tag{5}
$$

Studies on the concentrations of Ca^{2+} , Mg^{2+} , Na^{+} , K^{+} , HCO_3^- , Cl^-, SO_4^{2-} , NO_3^- and F^- ions derived from lithological and non-lithological sources have been carried out in different parts of the country (Jacks, 1973; Bilas, 1980; Bhatt and Saklari, 1996; Rajmohan et al., 1997; Elampooranan et al. 1999; Singh et al. 2000; Kumar et al. 2001; Subba Rao, 2002; Umar and Absar, 2003; Khurshid and Zaheerudin, 2004; Reddy and Prasad, 2005; Subba Rao et al. 2005; 2007; 2012; Rajmohan and Elango, 2006; Umar et al. 2006; John Devadas et al. 2007; Kumar et al. 2007; Manusree et al. 2009; Gupta et al. 2008; Naik et al. 2009; Ramachandramoorthy et al. 2009; Chidambaran et al. 2010; Goyal et al. 2010; Reddy and Niranjan Kumar, 2010; Mridul et al. 2011).

Mean values of pre- and post-monsoon chemical data of groundwater for the clusters distinguished by hierarchical cluster analysis are presented in Table 3. They show some trend between the major clusters A and B. Relatively, the cluster A, with the highest number of samples (93%), is characterized by high pH (7.78 to 7.84), HCO_3^- (612 to 672 mg/l), NO_3^- (35 to 37 mg/l) and F^{-} (1.19 to 1.33 mg/l), and low Ca²⁺ (50 to 53 mg/l), Mg²⁺ (46 to 54 mg/l), Na⁺ (284 to 354 mg/l), K⁺ (14 to 19 mg/l), Cl[–] (260 to 363 mg/l) and SO_4^{2-} (54 to 60 mg/) compared to

Table 2. Statistical summary of the chemical data of pre- and postmonsoon groundwater

Parameter	Monsoon Season	Min	Max	Mean	Std. Dev.	Coeff. of Variation
pH (units)	Pre	7.1	8.2	7.73	0.34	4.40
	Post	7.1	8.2	7.79	0.33	4.24
Ca^{2+} (mg/l)	Pre	30	75	51.67	13.15	25.45
	Post	35	75	54.17	10.01	18.48
$Mg^{2+} (mg/l)$	Pre	25	80	47.87	12.89	26.93
	Post	30	115	57.17	18.32	32.04
$Na^+(mg/l)$	Pre	192	648	305.93	110.34	36.07
	Post	159	883	385.73	177.94	46.13
$K^+(mg/l)$	Pre	10	38	18.97	6.16	32.47
	Post	8	23	13.73	4.17	30.37
$HCO3- (mg/l)$	Pre	370	890	596.00	134.26	22.53
	Post	400	970	653.83	161.73	24.74
$Cl^{-} (mg/l)$	Pre	130	1,045	308.33	199.38	64.66
	Post	140	1,470	430.17	294.46	68.45
SO_4^{2-} (mg/l)	Pre	21	145	59.50	27.90	46.89
	Post	23	170	66.70	33.46	50.16
NO_3^- (mg/l)	Pre	19	53	34.13	6.61	19.37
	Post	14	54	35.67	10.04	28.15
F^{-} (mg/l)	Pre	0.60	1.90	1.15	0.33	28.70
	Post	0.60	2.10	1.28	0.44	34.38

the cluster B, which shows the lowest number of samples (7%), having high Ca²⁺ (73 mg/l), Mg²⁺ (78 to 103 mg/l), Na⁺ (618 to 836 mg/l), K⁺ (16 to 20 mg/l), Cl⁻ (993 to 1,370 mg/l) and SO_4^{2-} (138 to 163 mg/l), and low pH (7.05 to 7.20), HCO_3^- (375 to 405 mg/l), NO_3^- (17 to 20 mg/l) and F⁻ (0.65 mg/l).

Sodium (222 to 618 mg/l) is the dominant ion among cations presemt in the groundwater of the sub-clusters I to V (Table 3). If Na⁺ is derived mainly from the rock weathering, the groundwater should have HCO_3^- as the most dominant anion (Rogers, 1989). It is true for the sub-clusters I to IV, as they show HCO_3^- as a dominant ion (508 to 863) mg/l) in the groundwater. The higher concentration of $HCO_3^$ reflects dominance of mineral dissolution (Stumm and Morgan, 1966). Further, it is also noticed that there is a difference in the concentration of HCO_3^- in the sub-clusters I to IV. For example, the higher concentration of HCO_3^- (863 mg/l) in the sub-cluster IV is observed in the lower elevated zone than that (508 mg/l) in the sub-cluster I of the upper elevated zone, following the drainage network. This is due to enhanced rate of chemical weathering from higher to lower topography, depending upon the rate of consumption of CO_2 in the rocks (Millot et al. 2002). The consumption of CO_2 released from the soil zone due to

decay of organic matter and root respiration acts as an important driving force of weathering rates, leading to a major mechanism for the occurrence of dissolved ions in the groundwater.

Spatial Distribution of Sub-clusters

To have a clear picture about the spatial relation of geochemical processes along the flow paths, the relationship of statistically defined pre- and post-monsoon groundwater samples of the sub-clusters to geographical location is shown in Figs.5 and 6. The less mineralized $(Ca^{2+}$: 43 mg/l; Mg²⁺: 40 mg/l; Na⁺: 222 mg/l; K⁺: 17 mg/l; HCO₃: 508 mg/l; Cl⁻: 195 mg/l; SO_4^{2-} : 49 mg/l; NO_3^- : 32 mg/l and F⁻: 0.98 mg/l; Table 3) pre-monsoon groundwater of the sub-cluster I (samples 1 to 7, 9, 10, 13, 15 and 22; Fig. 3) is observed from the northern part (upstream) and the highly mineralized $(Ca^{2+}$: 73 mg/l; Mg²⁺: 78 mg/l; Na⁺: 618 mg/l; K⁺: 20 mg/ l; HCO₃: 375 mg/l; Cl⁻: 993 mg/l; SO $_4^{2}$: 138 mg/l; NO₃: 20 mg/l and F: 0.65) pre-monsoon groundwater of the subcluster V (samples 29 and 30) from the extreme southeastern part (downstream). The medium mineralized $(Ca^{2+1}$: 47 to 73 mg/l; Mg²⁺: 43 to 57 mg/l; Na⁺: 271 to 436 mg/l; K⁺: 20 to 23 mg/l; HCO₃: 574 to 863 mg/l; Cl⁻: 250 to 402 mg/l; SO_4^{2-} : 49 to 86 mg/l; NO₃: 36 to 39 mg/l and F⁻: 1.22 to 1.73 mg/l) pre-monsoon groundwater of the sub-cluster II (samples 8, 11, 17, 23 and 24) occurs in the northeastern, central and southern parts; the sub-cluster III (samples 12, 14, 16, 18 to 21 and 25) in the eastern, western and southern parts; and the sub-cluster IV (samples 26 to 28) in the southern part of the area. On the other hand, very less mineralized (Ca²⁺: 52 mg/l; Mg²⁺: 32 mg/l; Na⁺: 178 mg/l; K⁺: 10 mg/l; HCO₃: 463 mg/l; Cl⁻: 165 mg/l; SO₄²-: 27 mg/ l; $NO₃⁻$: 22 mg/l and F⁻: 0.70 mg/l; Table 3) post-monsoon groundwater of the sub-cluster I (samples 1, 2 and 4; Fig. 4) is observed from the extreme upstream area (extreme northern part) compared to those of the pre-monsoon groundwater of the sub-cluster I and very highly mineralized post-monsoon groundwater (Ca^{2+} : 73 mg/l; Mg²⁺: 103 mg/ l; Na⁺: 836 mg/l; K⁺: 16 mg/l; HCO₃: 405 mg/l; Cl⁻: 1,370 mg/l; SO_4^{2-} : 163 mg/l; NO_3^- : 17 mg/l and F⁻: 0.65 mg/l) of the sub-cluster VI (samples 29 and 30) from the extreme southeastern part (downstream), as in the case of the premonsoon groundwater of the sub-cluster V. The medium mineralized post-monsoon groundwater $(Ca^{2+}$: 45 to 69 mg/ l; Mg^{2+} : 50 to 71 mg/l; Na⁺: 259 to 604 mg/l; K⁺: 12 to 20 mg/l; HCO₃: 573 to 930 mg/l; Cl⁻: 268 to 648 mg/l; SO $_4^{2-}$: 48 to 96 mg/l; NO₃: 32 to 44 mg/l and F⁻: 1.05 to 1.86 mg/ l) of the sub-cluster II (samples 3, 5 to 7, 9, 14, 15 and 18) occurs in the northeastern, central and western parts, while the sub-cluster III (samples 8, 10 to 13, 16, 17 and 22 to 24)

Table 3. Mean values of pre-and post-monsoon chemical data of groundwater for the clusters distinguished by hierarchical cluster analysis

Cluster	pH (units)	Ca^{2+} (mg/l)	Mg^{2+}	$Na+$	K^+	HCO ₂	Cl^-	SO_4^{2-}	NO_3^-	F^-	Percent of samples
Pre-monsoon											
Major cluster											
А	7.78	50.18	45.75	283.64	18.93	611.79	259.46	53.93	35.14	1.19	93.33
B	7.05	72.50	77.50	618.00	19.50	375.00	992.50	137.50	20.00	0.65	6.67
Sub-cluster											
Ι	7.53	42.92	40.08	222.00	16.50	507.92	194.58	48.83	31.67	0.98	40.00
$\mathbf I$	7.92	47.00	43.00	270.80	21.40	574.00	250.00	49.40	36.20	1.22	16.66
Ш	7.94	54.38	51.88	327.13	19.50	696.88	309.38	52.50	39.38	1.28	26.67
IV	8.17	73.33	56.67	435.67	23.00	863.33	401.67	85.67	36.00	1.73	10.00
V	7.05	72.50	77.50	618.00	19.50	375.00	992.50	137.50	20.00	0.65	6.67
Post-monsoon											
Major cluster											
А	7.84	52.86	53.93	353.57	13.61	671.61	363.04	59.86	37.04	1.33	93.33
B	7.20	72.50	102.50	836.00	15.50	405.00	1,370.00	162.50	16.50	0.65	6.67
Sub-cluster											
I	7.43	51.67	31.67	178.00	9.67	463.33	165.00	27.00	21.67	0.70	10.00
$\mathbf I$	7.79	45.00	50.00	258.75	12.13	573.13	267.50	47.88	32.25	1.05	26.67
Ш	7.85	52.00	53.50	345.70	13.50	762.00	346.00	64.90	42.50	1.37	33.33
IV	8.00	56.67	65.00	474.67	13.00	796.67	493.33	59.33	44.33	1.86	10.00
V	8.01	68.75	71.25	603.75	20.25	930.00	647.50	96.25	38.00	1.85	13.33
VI	7.20	72.50	102.50	836.00	15.50	405.00	1,370.00	162.50	16.50	0.65	6.67

occurs in the eastern, central, western and southern parts; the sub-cluster IV (samples 19 to 21) in the eastern and southwestern parts; and the sub-cluster V (samples 25 to 28) in the southern part of the area. Therefore, the spatial distribution of the sub-clusters indicates that the variations of groundwater quality from pre- to post-monsoon is responsible for shifting of groundwater samples from one sub-cluster to another due to influx of additional concentrations of ions in the infiltrating recharge water by the process of leaching.

Further, the various chemical concentration levels are observed to be low $(Ca^{2+1} : 43 \text{ mg/l}; Mg^{2+1} : 40 \text{ mg/l}; Na^+ : 222 \text{ mg/l}$ mg/l; K⁺: 17 mg/l; HCO₃: 508 mg/l; Cl⁻: 195 mg/l; SO $_4^{2-}$: 49 mg/l; NO_3^- : 32 mg/l and F^- : 0.98 mg/l) in the sub-cluster I compared to those of the concentrations $(Ca^{2+1}$: 47 to 73 mg/l; Mg²⁺: 43 to 78 mg/l; Na⁺: 271 to 618 mg/l; K⁺: 20 to 23 mg/l; HCO₃: 574 to 863 mg/l; Cl⁻: 250 to 993 mg/l; SO₄²: 49 to 138 mg/l; NO₃: 37 to 39 mg/l and F⁻: 1.22 to 1.73 mg/l) in the remaining sub-clusters II to V (excluding the concentrations of HCO₃: 375 mg/l; NO₃: 20 mg/l and F⁻: 0.65 mg/l in the sub-cluster V) of the pre-monsoon groundwater (Table 3). That too, the quality of groundwater of the sub-cluster I is observed from the upstream area (Fig. 5). Thus, this quality of groundwater is taken into consideration to assess the factors that are responsible for variations in the concentration levels of ions in the remaining sub-clusters (II to V).

The higher valuess of pH (7.92 to 8.17), Ca^{2+} (47 to 73) mg/l), Mg^{2+} (43 to 57 mg/l), Na^{+} (271 to 436 mg/l), K^{+} (20 to 23 mg/l), HCO_3^- (574 to 863 mg/l), $Cl^-(250 \text{ to } 402)$, SO_4^{2-} (49 to 86 mg/l), NO₃ (36 to 39 mg/l) and F⁻ (1.22 to 1.73 mg/l) in the sub-clusters II to IV than those of (pH; 7.53; Ca²⁺: 43 mg/l; Mg²⁺: 40 mg/l; Na⁺: 222 mg/l; K⁺ (17 mg/l: 195 mg/l; HCO₃: 503 mg/l; Cl⁻: 195 mg/l; SO₄²: 49 mg/l; NO₃: 32 mg/l and F⁻: 0.98 mg/l) in the sub-cluster I of pre-monsoon groundwater (Table 3) indicate clearly an induction of foreign matter in the sub-clusters II to IV of groundwater. This is caused by a water contamination, as the groundwater in the sub-clusters II to IV is observed from the immediate vicinity of the anthropogenic sources and/or along the flow paths of polluted surface water. The ions Mg^{2+} , Na⁺, Cl⁻, SO₄² and NO₃⁻ are indicative of man-made pollution caused by the domestic wastes, and the ions Na⁺, Cl⁻, SO₄², NO₃ and F⁻ by the agricultural activities (Todd, 1980; Hem, 1991). Further, the F⁻ ion is also derived from the lithological source, but the influence of chemical fertilizers appears to be more than that of the former in the study area. Thus, the concentration of F– in the sub-clusters II to IV is observed to be more than that in the sub-cluster I. Here, the local environmental conditions appear to play an important role. For example, the groundwater contamination of isolated distribution of the sub-cluster II in the northeastern, central and southern parts within the zones of sub-clusters I and III of pre-monsoon season (Fig. 5) is a

local phenomenon, which occurs along the surface flow paths of the sources of anthropogenic origin. Similarly, the local groundwater contamination is also seen in the subcluster III of post-monsoon, following the drainage conditions, as the groundwater of this sub-cluster is spread in the western part within the sub-cluster II, while those observed from the eastern and southwestern parts of the subcluster IV within the sub-clusters II and III of the area (Fig. 6). That means the higher chemical quality of groundwater of the sub-clusters is observed within the lower chemical quality of the sub-clusters or *vice-versa*. If the contamination of groundwater is uniform in the entire study area, such local variations in the chemical quality of groundwater may not be possible. Further, it is also noted that the spatial distribution of the sub-clusters on a regional scale suggests that there is a progressive enrichment of ions in the groundwater from higher to lower topography. Therefore, this indicates clearly the local modifications of the regional processes over the control of the various concentration levels of ions in the groundwater system.

Fig.5. Spatial distribution of pre-monsoon sub-clusters **Fig.6.** Spatial distribution of post-monsoon sub-clusters

The sub-cluster V of pre-monsoon groundwater shows higher concentrations of Cl⁻ (993 mg/l), Na⁺ (618 mg/l), $SO_4^{2-}(138 \text{ mg/l})$ and $Mg^{2+}(78 \text{ mg/l})$ than those of Cl⁻ (195 to 402 mg/l); Na⁺ (222 to 436 mg/l) SO_4^{2-} (49 to 86 mg/l) and Mg^{2+} (40 to 57 mg/l) in the sub-clusters I to IV (Table 3). Generally, the groundwater is dominated by $HCO₃⁻$ ion and the sea water by Cl⁻ ion. The groundwater samples 29 and 30 of the sub-cluster V are collected from the marine clay zone (Figs. 1 and 2). The ratio Na^{2+} : Cl⁻shows less than one (0.96; Table 5), with the high concentrations of Mg^+ (78 mg/l) and SO_4^{2-} (138 mg/l), and the low concentration of HCO_3^- (375 mg/l) in the groundwater of the sub-cluster V, while it is more than one (1.69), with the high concentration of HCO_3^- (508 to 863 mg/l), and the low concentrations of Mg²⁺ (40 to 57 mg/l) and SO_4^{2-} (49 to 86 mg/l) in the sub-clusters I to IV. Similarly, the ratio HCO_3^- : Cl^- is observed to be higher than one (1.37) in the subclusters I to IV, while it is found to be less than one (0.22) in the sub-cluster V. Thus, the differences in the distribution of ions between the sub-cluster V and the sub-clusters I to IV can lead to a higher mineralization of groundwater in the former cluster than in the latter ones due to influence of marine source in the groundwater.

Significantly, the concentrations of Mg^{2+} (103 mg/l), Na^{+} (836 mg/l), HCO₃ (405 mg/l), Cl⁻ (1,370 mg/l) and SO₄² (163 mg/l) in the post-monsoon groundwater of the subcluster VI (Table 4) are higher than those of Mg^{2+} (78 mg/ l); Na⁺ (618 mg/l); HCO₃ (375 mg/l) Cl⁻ (993 mg/l) and $SO_4^{2-}(138 \text{ mg/l})$ in the pre-monsoon groundwater of the subcluster V (Table 3). This is obviously expected due to leaching of ions from the pre- to post-monsoon groundwater. Further, the increasing concentrations of Mg^{2+} (from 78 to 103 mg/l), Na+ (from 618 to 836 mg/l), Cl– (from 993 to 1,370 mg/l) and SO_4^{2-} (from 138 to 163 mg/l) are more than the increasing concentrations of $HCO₃⁻$ (from 375 to 405 mg/l) from the pre- to post-monsoon groundwater between the sub-clusters V and VI, which also support the influence of marine origin on the groundwater. Therefore, the ratios Na^{2+} : Cl[–] and HCO₃: Cl[–] vary from 1.40 to 0.94 and 1.08 to 0.17 from pre- to post-monsoon groundwater, respectively (Table 4).

Ion exchange of Ca^{2+} by Na⁺ is also one of the factors for the higher concentration of Na in the groundwater, as the wells are in close proximity to the clay horizons formed by rock weathering (see Eq. 3). Thus, the ratio of Na⁺: Ca^{2+} varies from 4.94 to 10.05 in the major clusters A (sub-clusters I to V) and B (sub-clusters I to VI; Table 5), reflecting an ion exchange. Further, it is clearly observed that the ratio of Na⁺: Ca²⁺ is almost the same (4.94 to 5.83) in the cluster A (Table 4), indicating a common source of the ions, but it is different (7.43 to 10.05) in the cluster B, leading to an additional concentrations of ions to the existing ones from the different sources. Moreover, it is also noted that the ratio of Na⁺: Ca^{2+} is high (7.43) in the cluster B of pre-monsoon groundwater compared to those in the cluster A (4.44) of pre-monsoon groundwater, while it is higher (10.05) in the cluster B of post-monsoon groundwater than that in the cluster A (5.83) of post-monsoon groundwater. This indicates a higher concentration of Na⁺ in the post-monsoon groundwater due to leaching (Tables 3 and 4), which also supports the influences of anthropogenic and marine sources, higher contribution being from the latter in the groundwater.

As the groundwater is dominated by Na^+ , HCO_3^- , $Cl^$ and SO_4^{2-} ions compared to the remaining ions (Table 1), the saturation indices of $CaCO₃$, $CaSO₄$ and NaCl are computed to predict the mineral state whether it is in dissolved state or in saturated state or in precipitated state in water. A positive saturation index (2.61 to 3.13) of $CaCO₃$ reflects an oversaturated (precipitation) state and a negative

Pre-monsoon sub-clusters I to IV; ^ Post-monsoon sub-clusters I to V \$ Pre-monsoon sub-cluster V; &Post-monsoon sub-cluster VI

saturation index of $CaSO_4$ (-1.99 to -1.59) and NaCl (-1.64 to -1.59) an unsaturated (dissolution) state in the premonsoon groundwater (Table 5). The occurrence of *kankar*, as intercalation in the soil zone, supports the precipitation of $CaCO₃$ due to an active role of evaporation, which is a characteristic feature of the dry climatic condition. Further, the value of saturation index of $CaCO₃$ is observed to be high (3.13) in the cluster A (sub-clusters I to IV), where there is no contamination of groundwater by sea water compared to those (2.61) of the cluster B (sub-cluster V), where there is a contamination of groundwater by sea water. It is a known fact that the process of evaporation in saline environment is not as active as in non-saline environment, because of the higher salinity of sea water. Thus, it causes a variation in the values of saturation index of CaCO₂ between the uncontaminated groundwater and contaminated groundwater by the influence of sea water. Moreover, the groundwater contamination caused by the influence of marine source in the cluster B (sub-cluster V) shows more concentrations of Na⁺ (618 mg/l), Cl⁻ (993 mg/l) and SO₄² (138 mg/l) than those of Na⁺ $(222 \text{ to } 436 \text{ mg/l})$; Cl⁻ $(195 \text{ to } 436 \text{ mg/l})$ 402 mg/l) and SO_4^{2-} (49 to 86 mg/l) in the cluster A (subclusters I to IV) of pre-monsoon groundwater (Table 3). This reflects a dissolution state of saturation indices of NaCl (-1.59) and CaSO₄ (-1.59). On the other hand, the concentrations of Na⁺ (178 to 836 mg/l), HCO₃ (405 to 930) mg/l), Cl⁻ (165 to 1,370 mg/l) and SO₄⁻ (27 to 163 mg/l) in the post-monsoon groundwater (Table 3) are higher than the concentrations of Na⁺ (222 to 618 mg/l); HCO₃ (375 to 863 mg/l); Cl⁻ (195 to 993 mg/l); and SO²⁻ (49 to 138 mg/ l) in the pre-monsoon groundwater, resulting from the low values of saturation indices of CaCO₃ (2.15 to 2.18), CaSO₄ (-1.84 to -1.41) and NaCl (-1.56 to -1.39). Therefore, the

Table 5. Saturation indices

			Saturation index			
Major	CaCO ₃		CaSO ₄		NaCl	
cluster	Pre	$Post**$	Pre	Post	Pre	Post
А		$3.13^{\#}$ 0.15° $-1.99^{\#}$ -1.84° $-1.64^{\#}$ -1.56°				
в	2.61 ⁸	0.18^{k}		$-1.59^{\$}$ $-1.41^{\&}$ $-1.59^{\$}$ $-1.39^{\&}$		

 $*$ Pre-monsoon sub-clusters I to IV^{\cdot}; Post-monsoon sub-clusters I to V \$ Pre-monsoon sub-cluster V; & Post-monsoon sub-cluster VI

saturation indices indicate clearly that the differences in the mineral dissolution and precipitation are responsible for the concentrations of dissolved ions in the water.

Because of the lithological and non-lithological influences, the concentration of Mg^{2+} (78 to 103 mg/l) in the groundwater is observed to be more than Ca^{2+} (73 mg/l) in the major cluster B of both the seasons (Table 3). But in the case of major cluster A, there is more Ca^{2+} (50 mg/l) than Mg^{2+} (46 mg/l) in the pre-monsoon groundwater and these two ions show more or less same concentration (around 53 mg/l) in the post-monsoon groundwater. This suggests that the input of additional concentration of Mg^{2+} into the groundwater from the nonlithological sources, especially from the marine environment, due to leaching during the post-monsoon season. Further, owing to adsorption of K^+ ion on clays, its concentration is found to be very low (13 to 20 mg/l) compared to the other cationic concentrations in both the clusters A and B.

Interestingly, the major cluster A is characterized by the high pH (7.78 to 7.84) and the high concentrations of $HCO₃⁻(612 to 672 mg/l)$ and $F⁻(1.19 to 1.32 mg/l)$ compared to those (pH: 7.05 to 7.20; HCO₃: 375 to 405 mg/l; and F⁻: 0.65 mg/l) in the major cluster B in both the seasons, being the higher values in the post-monsoon groundwater (Tables 3 and 4). It is clear from these observations that the high pH in the cluster A is possibly the most evolved groundwater in the area, while the high HCO_3^- is the most important factor to elevate the concentration of F– in the water from the source.

Major

Hydrogeochemical Facies

Hydrogeochemical facies reflect the response of chemical processes in a lithological framework and the pattern of water flow in it, as it explains the distribution and genesis of groundwater types along the water flow paths (Seaber, 1962; Back, 1966).

In the present study, it is observed that the sub-clusters I to IV show $\text{Na}^+ > \text{Mg}^{2+} > \text{Ca}^{2+} > \text{K}^+$: $\text{HCO}_3^- > \text{Cl} > \text{SO}_4^{2-}$ $>NO_3^-$ > F⁻ facies, while the sub-clusters V has Na^+ > Mg^{2+} $> Ca^{2+} > K^+$: Cl⁻> HCO₃ > SO₄² > NO₃ > F⁻ facies in premonsoon season (Table 7). On the other hand, the subclusters I to III represent Na^+ > Mg^{2+} > Ca^{2+} > K^+ : HCO_3^- > Cl⁻> SO_4^2 > NO₃ > F⁻ facies, while the sub-clusters IV to VI show the $Na^+ > Mg^{2+} > Ca^{2+} > K^+$: Cl⁻> HCO₃ > SO₄² > $NO₃⁻ > F⁻$ facies in post-monsoon season. That too, all the concentrations of ions of post-monsoon groundwater are more than those of the pre-monsoon groundwater due to leaching (Table 3).

Further, it is noted that the concentrations of Na⁺ (475) to 604 mg/l or 21 to 26 meq/l) is more than that of Cl^{-} (493 to 648 mg/l or 14 to 18 meq/l) in the sub-clusters IV and V of post-monsoon groundwater (Table 3), reflecting the dominance of rock-weathering, while the concentration of Cl⁻ is high compared to that of HCO_3^- (797 to 930 mg/l or 13 to 15 meq/l), with the higher concentrations of SO_4^{2-} (59 to 63 mg/l), NO_3^- (36 to 44 mg/l) and F^- (1.85 to 1.86 mg/l) in the sub-clusters IV and V, as in the sub-clusters II and III – : 32 to 44 mg/l; and F: 1.05 to

A Pre-monsoon Na⁺ $> Mg^{2+} > Ca^{2+} > K^+$: HCO– $\frac{1}{3}$ > Cl⁻ > SO₄ Post-monsoon Na⁺ $> Mg^{2+} > Ca^{2+} > K^+$: HCO– $\frac{1}{3}$ > Cl⁻ $> SO₄$ B Pre-monsoon Na⁺ $> Mg^{2+} > Ca^{2+} > K^+$: $CI^- > HCO_2^ _3^- > SO_4^2$ Post-monsoon Na⁺ $> Mg^{2+} > Ca^{2+} > K^+$ Γ : Cl⁻ > HCO₃ $_3^- > SO_4^2$ Sub-clu I Pre-monsoon Na+ $> Mg^{2+} > Ca^{2+} > K^+$: HCO– $\frac{1}{3}$ > Cl⁻ > SO₄ Post-monsoon Na⁺ $> Mg^{2+} > Ca^{2+} > K^+$: HCO– $\frac{1}{3}$ > Cl⁻ > SO₄ II Pre-monsoon Na+ $> Mg^{2+} > Ca^{2+} > K^+$: HCO– $\frac{1}{3}$ > Cl⁻ > SO₄ Post-monsoon Na⁺ $> Mg^{2+} > Ca^{2+} > K^+$: HCO– $\frac{1}{3}$ > Cl⁻ > SO₄ III Pre-monsoon Na+ $> Mg^{2+} > Ca^{2+} > K^+$: HCO– $\frac{1}{3}$ > Cl⁻ > SO₄ Post-monsoon Na⁺ $> Mg^{2+} > Ca^{2+} > K^+$: HCO– 3 $> Cl^{-} > SO_{4}^{2}$ IV Pre-monsoon Na+ $> Mg^{2+} > Ca^{2+} > K^+$: HCO– 3 $>$ Cl[–] $> SO₄$ Post-monsoon Na⁺ $> Mg^{2+} > Ca^{2+} > K^+$: Cl– $>$ HCO₂ 3 $> SO₄$ V Pre-monsoon $> Mg^{2+} > Ca^{2+} > K^+$: Cl⁻ $> HCO_3^- > SO_4^{2-} > NO_3^- > F^-$ Post-monsoon $> Mg^{2+} > Ca^{2+} > K^+$: Cl⁻ $> HCO_3^- > SO_4^{2-} > NO_3^- > F^-$ VI Pre-monsoon $> Mg^{2+} > Ca^{2+} > K^+$: Cl⁻ $> HCO_3^- > SO_4^{2-} > NO_3^+ > F^-$ Post-monsoon $> Mg^{2+} > Ca^{2+} > K^+$: Cl⁻ $> HCO_3^- > SO_4^{2-} > NO_3^- > F^-$

1.37 mg/l), than in the sub-cluster I (HCO₃: 463 mg/l; Cl⁻: 165 mg/l; SO_4^{2-} : 27 mg/l; NO_3^{-} : 22 mg/l; and F⁻: 0.70 mg/l), resulting from the anthropogenic influence. Moreover, the concentration of Na^+ (618 to 836 mg/l or 27 to 36 meq/l) is less than that of Cl^- (993 to 1,370 mg/l or 28 to 36 meq/l) in the sub-clusters V and VI of the pre- and post-monsoon groundwater, respectively, indicating the chemistry of groundwater controlled by the marine source. Thus, the distribution of the facies in the sub-clusters obviously supports the views of the spatial variations in the quality of groundwater caused by the lithological and nonlithological factos, following the topography, as discussed above.

From the distribution of the facies on a regional scale, it is also observed that the quality of groundwater depends on the influence of lithology in all the sub-clusters of pre- and post-monsoon groundwater. Subsequently, it is modified by the anthropogenic sources in the sub-clusters II and V of pre-monsoon and II to VI of post-monsoon groundwater. Further, it is significantly masked by the marine influence

 $82^{0|}50$ $82^{0|}35$ 17° Vulnerable groundwater zones Very low vulnerable Low vulnerable Moderate vulnerable

 $\overline{2}$ $\overline{0}$ $2 km$

High vulnerable

Very high vulnerable

25

in the sub-cluster V of pre-monsoon and VI of post-monsoon groundwater. As a result, the groundwater characterized by $\text{Na}^+ > \text{Mg}^{2+} > \text{Ca}^{2+} > \text{K}^+$: $\text{HCO}_3^- > \text{Cl}^- > \text{SO}_4^2 > \text{NO}_3^- > \text{F}^$ facies in the sub-clusters I to IV and I to V of the major cluster A is changed to Na^+ > Mg^{2+} > Ca^{2+} > K⁺: Cl⁻ > HCO₃ $> SO_4^2$ $> NO_3^2$ $> F^-$ facies in the sub-cluster V and VI of the major cluster B of both the seasons, with a gradual increasing of the ions, in general, (Table 3 and 6), depending upon the availability of source, mineral dissolution and precipitation, solubility and leaching of ions, ion exchange and adsorption, following the topography.

Vulnerable Groundwater Zones

For planning remedial measures to improve the quality of groundwater, it is essential to delineate the relative vulnerability of groundwater zones. In the present study, the area is classified as non-vulnerable, very low vulnerable, low vulnerable,, moderate vulnerable, high vulnerable and very high vulnerable groundwater zones (Table 7; Figs. 7 and 8) on the basis of spatial distribution of the sub-

Fig.7.Vulnerable groundwater zones of pre-monsoon. **Fig.8.**Vulnerable groundwater zones of post-monsoon.

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Table 7. Classification of vulnerable groundwater zones with respect to the sub-clusters

Classification of vulnerable	Sub-clusters			
groundwater zones		Pre-monsoon Post-monsoon		
Non-vulnerable groundwater zone				
Very low vulnerable groundwater zone		Π		
Low vulnerable groundwater zone	Π	Ш		
Moderate vulnerable groundwater zone	Ш	IV		
High vulnerable groundwater zone	IV	V		
Very high vulnerable groundwater zone	V	VI		

clusters of pre- and post-monsoon seasons (Table 3) with respect to their drinking water quality standards. For example, the quality of groundwater in sub-cluster I of the post-monsoon is suitable for drinking compared to that of pre-monsoon groundwater. Therefore, the former sub-cluster comes under the category of non-vulnerable groundwater zone, while that of the latter is classified as very low vulnerable groundwater zone. Similarly, the chemical composition of the sub-cluster VI of the post-monsoon groundwater shows the higher concentrations of ions than those of the sub-cluster V of the pre-monsoon groundwater. In fact, the quality of water in both the sub-clusters is not suitable for drinking. In view of their relative quality of groundwater, the sub-cluster V of pre-monsoon is designated as high vulnerable groundwater zone and the sub-cluster of VI of post-monsoon as very high vulnerable groundwater zone. Similarly, the remaining sub-clusters II to IV of premonsoon and II to V of post-monsoon are classified as low to high vulnerable groundwater zones and as very low to high vulnerable groundwater zones, respectively. Thus, the classification of the area into the zones of groundwater vulnerability helps the planners for taking the appropriate management measures to improve the quality of groundwater for sustainable development of the area.

CONCLUSIONS

From this study, it is concluded that the quality of groundwater is fresh to brackish, the latter being the dominant. Two major clusters A and B are identified from the groundwater samples, using the dendrogram of cluster analyses. Five sub-clusters I to V are observed from the premonsoon groundwater samples and six sub-clusters I to VI from the post-monsoon groundwater samples forming the major clusters A and B. The sub-clusters I to IV of premonsoon season and I to V of post-monsoon season of the cluster A have a less mineralized groundwater compared to the sub-cluster V of pre-monsoon and VI of post-monsoon season of the cluster B, which shows a highly mineralized groundwater. Further, the spatial distribution of the subclusters helps distinguishing the groundwater vulnerability at a specific site, depending upon the mineral dissolution and precipitation, solubility and leaching of ions, ion exchange and adsorption processes in relation to the lithological and non-lithological sources, following the topographic gradient. Therefore, the quality of groundwater is characterized by $\text{Na}^+ > \text{Mg}^{2+} > \text{Ca}^{2+} > \text{K}^+$: $\text{HCO}_3^- > \text{Cl}^ SO_4^{2-} > NO_3^- > F^-$ facies in the cluster A and by $Na^+ > Mg^{2+}$ $> Ca^{2+} > K^+$: Cl⁻> HCO₃ > SO₄² > NO₃ > F⁻ facies in the cluster B. These observations give a clear picture of the local and regional variations of the groundwater vulnerability. The area is classified into zones of relative groundwater vulnerability based on the drinking water quality standards vis-a-vis the chemical composition of the sub-clusters for helping the planning authorities for implementing the remedial measures at appropriate locations to improve the water quality.

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