

Application of Multivariate Statistical Techniques for the Characterization of Groundwater Quality of Bacheli and Kirandul Area, Dantewada District, Chattisgarh

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ABSTRACT

Either naturally occurring process or human activities may have a significant impact on the quality of sub-surface waters which further limit its use. Multivariate statistical techniques such as factor analysis (FA), cluster analysis (CA) were applied for the evaluation of spatial variations and the interpretation of ground water quality data around Bacheli and Kirandul area. The major anions, cations and heavy metals were determined for each of 20 samples collected in pre-monsoon seasons. Hydrochemical parameters like EC, pH, TDS, TH, TA, Na^+ , K^+ , Ca^{2+} , Cl^- , F^- , SO_4^{2-} , As, Sb, Se, Pb, Cd, Zn, Cu were estimated in pre monsoon and post monsoon seasons. Different geochemical controls of the investigated parameters were also assessed. Factor 1 explains 33.47% of the total variance and indicates atmospheric controls and silicate mineral weathering process. Factor 2 explains 13.83% of total variance, indicating silicate mineral weathering process resulting in elevated pH. Generally, water types tend towards magnesium-bicarbonate-chloride.

INTRODUCTION

During the past decades, the water level in several parts of India has been falling rapidly due to increase in extraction (Gupta and Deshpande, 2004). Groundwater quality variation is a function of physical and chemical patterns in an area influenced by geological and anthropogenic activities (Subramani et al. 2005). Groundwater quality gets altered when it moves along its flow path from recharge to discharge areas through the process like: evaporation, transpiration, selective uptake by vegetation, oxidation/reduction, cation exchange, dissociation of minerals, precipitation of secondary minerals, mixing waters, leaching of fertilizers, manure and biological process (Appelo and Postma, 1993). The chemical quality of the groundwater percolating through the soil zones of anthropogenically polluted layers, are significantly reduced.

Groundwater is the major source of drinking water in both urban and rural areas. Groundwater is also frequently used as the alternative source for agricultural and industrial sector (A. Mishra et al., 2008). Distribution of groundwater quality parameters is controlled by complex processes. The groundwater quality depends not only on natural factors such as the lithology of the aquifer, the quality of recharge water and the type of interaction between water and aquifer, but also on human activities which can alter these groundwater systems either by polluting them or by changing the hydrological cycle (Helena et al. 2000). Water quality monitoring is one of the top priorities in environmental protection policy (Simeonov et al., 2000). A monitoring program that provides a repetitive and reliable estimation of the quality of groundwater has become an important necessity. Consequently monitoring programs that include frequent water sampling at numerous sites and complete analysis of a large number of physicochemical parameters

are to be designed for proper management of water quality of groundwaters.

In order to avoid this problem multivariate methods such as the factor analysis, cluster analysis and discriminant analysis were used. The application of multivariable statistical methods offer a better understanding of water quality for interpreting the complicated data sets.

The specific objectives of present study are to (1) extract latent information about the quality of groundwater, (2) classification of sampling stations of each site, (3) extract the parameters that are most important in assessing variations in groundwater quality.

EXPERIMENTAL

Study Area

The Bacheli and Kirandul areas of Dantewada district are 420 km away from Raipur, the capital city of Chhattisgarh, India. The two places are located at 18°42'19"E longitude and 81°15'7"N latitude. The Dantewada district is spread over 9,046.29 km². Asia's biggest iron ore reservoirs are present in these areas and on surface these two places are covered fully with iron ore. So, this survey is of importance as it would show the impact of iron ore on the groundwater quality.

The different places under observations are: (1) Arya hospital (S-1), (2) Gayatri Bhawan (S-2), (3) Guest house (S-3), (4) Intac complex market (S-4), (5) Ghadi chhak (S-5) (6) Bade bachelis (S-6), (7) Mundra camp (S-7), (8) Old market (S-8), (9) Old Double story (S-9), (10) Bharatpur camp (S-10), (11) Mundra camp Kirandul (S-11), (12) Singar pur camp (S-12), (13) Rampur camp (S-13), (14) Railway colony (S-14), (15) Bus stands (S-15), (16) Mishra camp (S-16), (17) Foot Ball Ground (S-17), (18) Ora camp (S-18), (19) Mandir para (S-19), (20) Main road (S-20).

MATERIALS AND METHODS

The samples were collected from the bore wells for different seasons representing pre-monsoon to broadly cover the seasonal variation. A total of 20 groundwater samples were collected in one litre acid washed, well rinsed low density polyethylene bottles with inside stopper from bore wells and analysed for chemical parameters using the standard guidelines (APHA, 1995). The samples were collected after pumping the wells for 5-10 min and by subsequent filtering through 0.45 µm membranes. The temperatures of the samples were noted at their sampling points itself. The analysed parameters include hydrogen ion concentration (pH), electrical conductivity (EC), turbidity, total hardness (TH), total dissolved solids (TDS) and important cations like sodium (Na^+), Potassium (K^+), Calcium (Ca^{2+}), Magnesium (Mg^{2+}) and anions like bicarbonate (HCO_3^-), Chloride (Cl^-), Nitrate (NO_3^-), Sulphate (SO_4^{2-}), Fluoride (F^-). The pH and electrical conductivity were measured using pH and EC meter. Calcium (Ca^{2+}) and magnesium (Mg^{2+}) were determined titrimetrically using

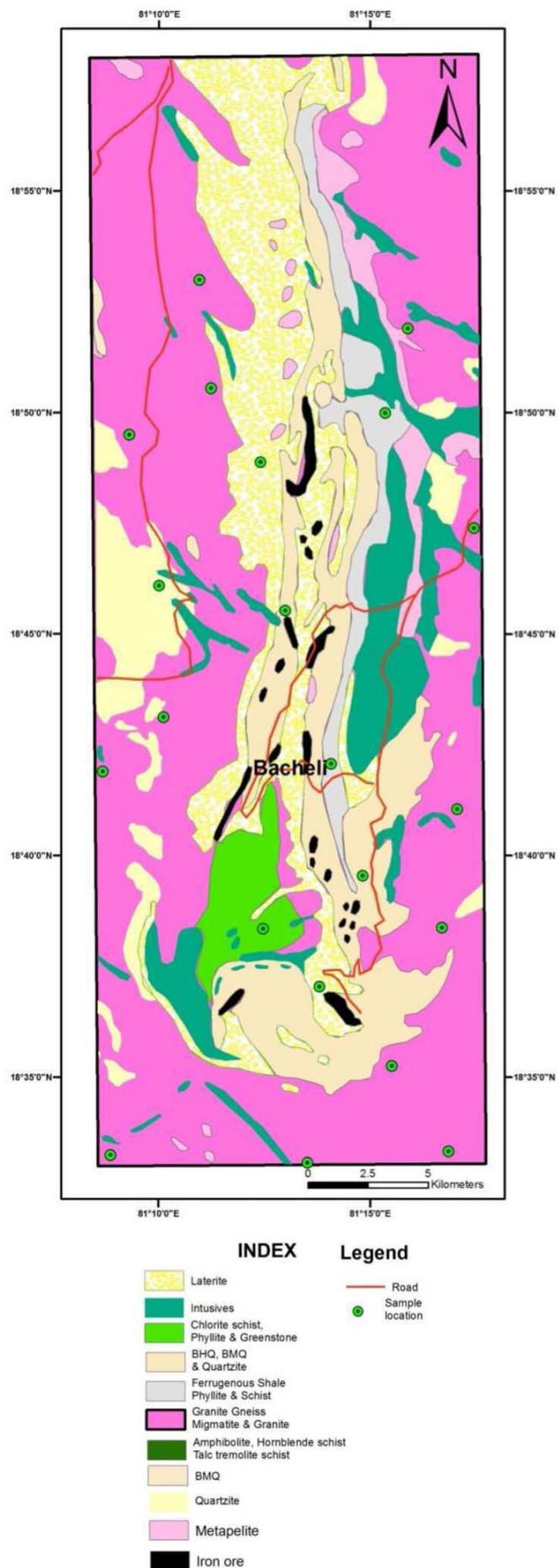


Fig 1. Geological and sample location map of Bacheli and Kirandul area of topo sheet no.65F (part)

standard EDTA. Chloride (Cl^-) was analysed by standard AgNO_3^- titration. Bicarbonate (HCO_3^-) by titration with H_2SO_4 . Sodium (Na^+) and potassium (K^+) measured by flame photometer, sulphate by turbidity method by turbido meter. Fluoride (F^-) by Ion selective electrode, Nitrate (NO_3^-) by colorimeter by Agilent carry make. Total dissolved solids (TDS) were measured by evaporation and calculation methods (Hem, 1991). Concentrations of heavy metals in water samples were determined by Atomic Absorption Spectroscopy. Quality control of analytical data was under taken by routinely analysing blanks, duplicate and standards and by checking ion balances. The ionic charge balance error was within 5%.

RESULTS AND DISCUSSION

Factor Analysis

The multivariate statistical analysis is widely used to characterize and assess the groundwater quality and it is used for evidencing temporal and spatial variations caused by natural and human factors linked to seasonality (Kaiser et al., 1958; Halena et al., 2000; Huang et al., 2005). Factor analysis assumes that relationships within a set of variables reflects correlations with a smaller number of underlying factors (Davis et al. 1973). The main applications of factor analytical techniques are to reduce the number of variables and to detect structure in the relationships between variables, or to classify them. A special feature of this technique is that it extracts factors or principal components which are linear combinations of all variables that can explain the maximum of total variance, the remaining factors define the maximum of the residual variability. The factors extracted are uncorrelated or orthogonal to each other. The variances extracted by the factors are called the eigen values. Since the first factors explain maximum variance it has the highest eigen value. The sum of eigen values of all factors will be equal to the total number of variables. In this way only those factors which have eigen values >1 have been selected. The correlations of the original variables in the factors extracted are termed as factor loadings. To obtain a clear pattern of loadings and to maximize the variance on the first extracted principal axes, the varimax normalized rotation was applied (Schot et al., 1992; Jayakumar et al., 1997; Adams et al., 2001; Aiuppa, 2003).

Cluster Analysis

Cluster analysis (CA) is a statistical tool to classify the true groups of data according to their similarities to each other. All variables were also standardized by Z-score mode before being subjected to CA. A short Euclidean distant implies the high similarity between the measured objects. In clustering, the distinct groups can reveal either the interaction among the variables (R-mode) or the interrelation among the samples (Q-mode) (Wu et al., 2005). Two types of CA methods, hierarchical cluster analysis and non-hierarchical cluster analysis, have been performed in two-step procedures in this study. Ward's clustering procedure commonly used in hierarchical method of cluster analysis was employed to identify the number of clusters. Next, the non-hierarchical cluster analysis was utilized to obtain the correct classified observations by K-mean method. A multivariate analysis including factor analysis and CA was conducted by the computer software package named as Stat soft statistica v.7.0.61.0 with crack.

In the pre-monsoon season, factor analysis displayed most of the variables loadings in the first factor itself (EC, TDS, Ca, Na, total hardness, total alkalinity and dissolved oxygen)

Factor 1

In factor 1, 33.47% of the total variance with high positive loading on EC, TDS, Ca^{2+} , Na^+ , total hardness, total alkalinity, K^+ which were 0.950, 0.947, 0.925, 0.908, 0.826, 0.750, 0.677 respectively. High positive loadings indicated strong linear correlation between the

Table 1. Descriptive statistics of water quality data from Bacheli and Kirandul area

	pH	EC	TDS	Turbidity	TA	TH	Mg ²⁺	Na ⁺	K ⁺	Ca ²⁺
Minimum	6.08	320	160	0	64	98	4	4.9	0	6.8
Maximum	6.92	3430	1700	637	264	505	12.66	67.5	4.3	21.1
Mean	6.646	853.2	431.2	63.451	147.3	232.35	8.913	15.815	1.75	6.475
Median	6.665	637.5	341.5	4.9	152	225	9.5	13.5	1.65	11.2
Std.Devi.	0.198	661.27	326.47	152.57	52.80	85.73	2.43	13.00	1.18	17.07
Coeff.of var.	2.98	77.50	75.71	240.45	35.85	36.90	27.30	82.25	67.22	103.6
	DO	SO ₄ ⁻²	Cl ⁻	F ⁻	Sb	As	Se	Pb	Cd	Zn
Minimum	2.38	48	126	0	0	0	0	0.016	0.019	0.026
Maximum	5.25	400	294	0.17	0.19	38.7	0.82	0.61	3.137	6.124
Mean	3.543	211.1	191.65	0.056	0.034	4.77	0.18	0.103	0.558	0.629
Median	3.27	194	176.5	0.05	0	1.27	0.1	0.06	0.335	0.235
Std.Devi.	1.089	91.671	46.556	0.044	0.064	9.139	0.236	0.138	0.716	1.341
Coeff.of var.	30.76	43.425	24.292	78.246	191.65	191.66	127.71	132.62	128.39	213.07

(Units of parameters represented as EC=µS/cm, The unit of TDS, Total Alkalinity(TA), Total hardness (TH), Mg²⁺, Na⁺, K⁺, Ca²⁺, DO, SO₄⁻², Cl⁻, F⁻, Pb, Zn are represented as mg/L. Units of Sb, As, Se, Cd are represented as µg/L)

factor and parameters. Thus factor 1 can be termed as salinization factor. The electrical conductivity (EC) is positively correlated with the concentration of ions, which can thus be directly calculated from EC. Therefore, EC can be regarded as a water salinization index. The EC value varies from 320 mg/L to 3430 mg/L with average value 853.2 mg/L. The high loading in conductance may be due to contamination of conducting materials in ground water. The higher loading of Na⁺, K⁺, Ca²⁺ present in ground water shows that leaching and dissolution of secondary salts in the pore spaces. Total alkalinity of ground water may be due to carbonate and bicarbonate, hydroxide of Na. The TDS value varies from 160 mg/L to 1700 mg/L with mean value 431.2 mg/L. It may be due to rocky nature containing several minerals and total hardness value varies from 98 mg/L to 505 mg/L with mean 232.35 mg/L which may be due to soluble of calcium and

magnesium salts. These salts enter into water sources from geological deposits through which water travels for a longer period of time than surface water.

Factor 2

Factor 2 of the pre-monsoon samples are represented mainly Zn,

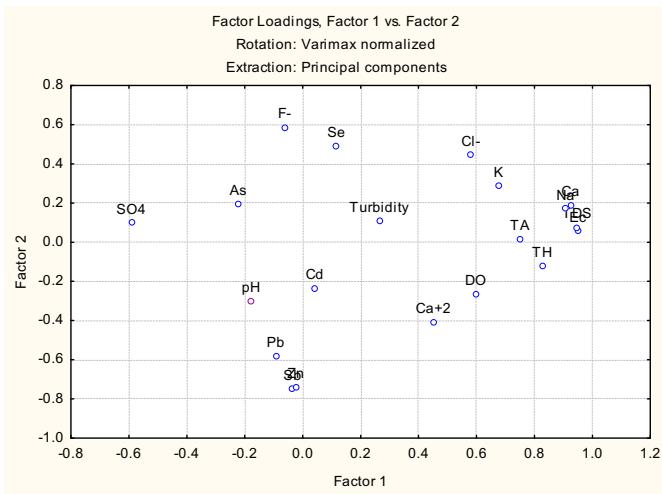


Fig.2. Scatter diagram of factor 1 vs factor 2 for groundwater in study area.

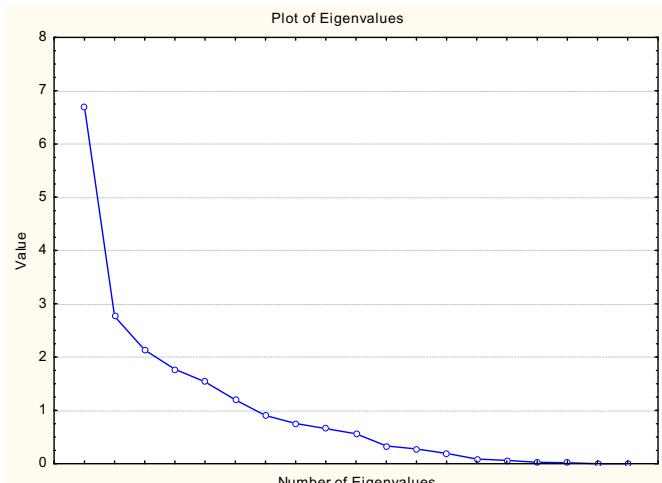


Fig.3. Scree plot of the Eigen value.

Sb having negative and fluoride having positive loading value. The value of zinc varies from 0.026 ppm to 6.124 ppm while concentration of antimony varies from 0 ppb to 0.19 ppb. The concentration of fluoride varies from 0 ppm to 0.17 ppm. Fluoride in groundwater is basically from minerals of rocks.

There are 19 monitoring location identified within cluster 1. The groundwater quality in cluster 1 is better as compared with other clusters. The high level of EC and TDS, turbidity, Ca^{2+} (hardness), SO_4^{2-} , Sb, As, Pb, Cd, Zn are observed in cluster 2 while total alkalinity, K, dissolved oxygen, F⁻, Cl⁻, Se are observed in cluster 3. It is observed that groundwater quality of cluster 2 is bad in the study region. There is only one monitoring well identified in cluster 2. Therefore, high level of EC, turbidity, TDS, As are observed in cluster 2 whose groundwater quality was bad in the study water. The sample station no. 20 is highly polluted than sampling station no. 19 and than all the sampling stations.

Correlation of Physicochemical Parameters of Groundwater

In order to find out the relationship amongst physicochemical parameters of the water samples, correlation coefficients were

Table 3. Chemical properties of each cluster classified by K-mean method

Vari- able	Unit	Cluster1	Cluster2	Cluster 3
pH	mean	0.052	0.060	0
	range	0.010-0.130	0.020-0.100	0
EC	mean	101.43	121.52	0
	range	31.385-239.38	14.60-180.60	0
TDS	mg/L (mean)	54.876	64.88	0
	mg/L (range)	16.385-126.615	15.4-108.4	0
Turbi- dity	NTU (mean)	12.186	76.50	0
	NTU (range)	2.635-33.438	76.50	0
TA	mg/L (mean)	9	12	17
	mg/L (range)	4-28	3-29	6-35
TH	mg/L (mean)	31.259	24.889	0
	mg/L (range)	10.444-71.556	12.00-63.00	0
Mg ²⁺	mg/L (mean)	0.855	0.727	0.200
	mg/L (range)	0.054-2.054	0.286-1.314	0.200
Na ⁺	mg/L (mean)	2.259	1.602	0
	mg/L (range)	0.622-7.422	0.378-4.578	0
K ⁺	mg/L (mean)	0.281	0.225	0.300
	mg/L (range)	0.033-0.733	0.050-0.450	0.300
Ca ²⁺	mg/L (mean)	1.100	1.816	0
	mg/L (range)	0.140-3.140	0.012-4.088	0
DO	mg/L (mean)	0.213	0.409	0.545
	mg/L (range)	0.043-0.457	0.123-0.777	0.545
SO ₄ ²⁻	mg/L (mean)	19.407	38.50	4.00
	mg/L (range)	2.667-31.333	16.00-96.00	4.00
Cl ⁻	mg/L (mean)	13.219	14.556	16.480
	mg/L (range)	0.375-23.625	4.167-21.833	4.600-6.600
F ⁻	mg/L (mean)	0.009	0.010	0.024
	mg/L (range)	0.000-0.020	0.000-0.020	0.003-0.048
Sb	ppb (mean)	0.003	0.016	0.015
	ppb (range)	0.001-0.019	0.007-0.023	0.015
As	ppb (mean)	1.157	5.090	0
	ppb (range)	0.013-3.493	5.090	
Se	ppb (mean)	0.054	0.090	0.085
	Ppb (range)	0.012-0.118	0.035-0.145	0.085
Pb	mg/L (mean)	0.022	0.090	0
	mg/L (range)	0.000-0.055	0.090	0
Cd	ppb (mean)	0.155	0.155	0
	Ppb (range)	0.026-0.235	0.071-0.238	0
Zn	mg/L (mean)	0.097	0.239	0
	mg/L (range)	0.005-0.225	0.013-0.584	0
Number of Sampling wells	1,2,3,4,5,6,7, 9,10,11,12,13, 14,16,17, 18,19, 20	8	0	

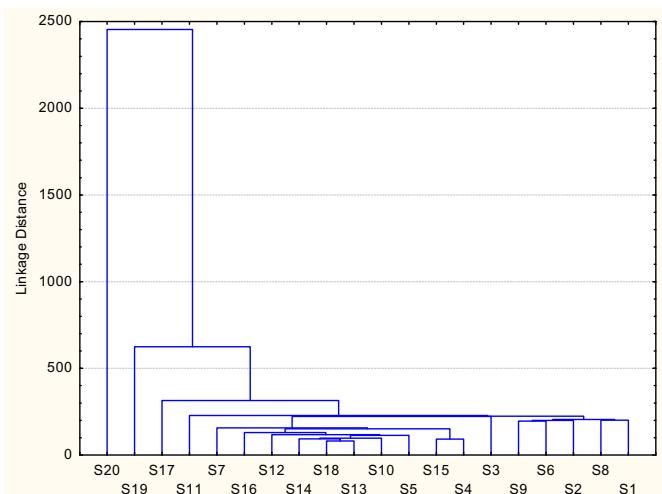


Fig.4. Vertical icicle plot of cluster analysis of groundwater quality of sampling stations.

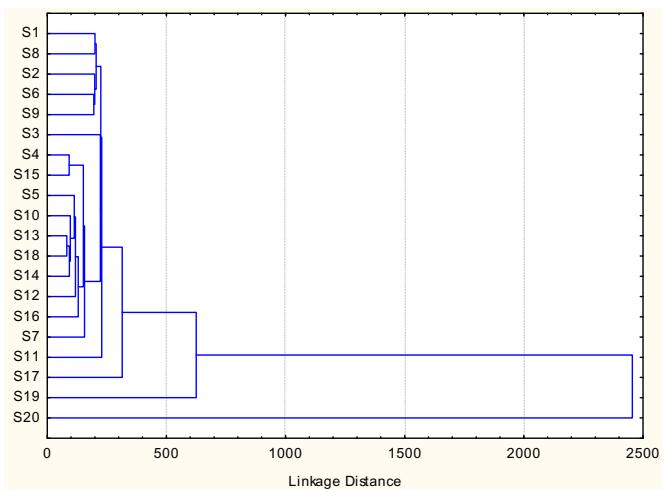


Fig.5. Dendrogram of the hierarchical cluster analysis of the groundwater quality of sampling stations.

calculated and a large number of significant correlations were obtained. Correlation is the mutual relationship between two variables. Direct correlation exists when increase or decrease in the value of one parameter is associated with a corresponding increase or decrease in the other. The correlation is said to be positive when increase in one parameter causes the increase in the other parameter and it is negative when increase in one parameter causes the decrease in the other. The correlation coefficient (r) has a value between +1 and -1. The correlation between the parameter is characterized as strong, when it is in the range of +0.8 to +1.0 and -0.8 to -1.0, moderate when it is having value of +0.5 to 0.8 and -0.5 to -0.8, weak when it is in the range of +0.0 to +0.5 and -0.0 to -0.5. Based on the literature review, the relationship of water quality parameters on each other in the samples of water analysed was determined by determining correlation coefficients (r) by using formula as given below. Let x and y be any two variables (water quality parameters in the present investigation) and n = number of observations. Then the correlation coefficient (r) between the variables x and y is given by the relation

$$r = \frac{n \sum (x * y) - \sum x * \sum y}{\sqrt{\sum (x^2) - (\sum x)^2} \sqrt{\sum (y^2) - (\sum y)^2}}$$

Where $\sum (x^2) = n \sum (x^2) - (\sum x)^2$ and $\sum (y^2) = n \sum (y^2) - (\sum y)^2$ and all the summations are to be taken from 1 to n .

Table 4. Correlation coefficient between quality parameter

	pH	EC	TH	Ca ²⁺	Na ⁺	K ⁺	DO	SO ₄ ²⁻	Cl ⁻	F ⁻	Sb	As	Se	Pb	Cd	Zn
pH	1.00															
EC	-0.28	1.00														
TH	-0.16	0.88	1.00													
Ca ²⁺	-0.20	0.29	0.32	1.00												
Na ⁺	-0.21	0.92	0.75	0.28	1.00											
K ⁺	0.10	0.52	0.34	0.28	0.60	1.00										
DO	0.06	0.51	0.54	0.25	0.37	0.40	1.00									
SO ₄ ²⁻	0.01	-0.51	-0.36	-0.19	-0.40	-0.43	-0.26	1.00								
Cl ⁻	-0.19	0.54	0.39	-0.09	0.53	0.51	0.22	-0.50	1.00							
F ⁻	-0.02	0.04	-0.07	-0.56	0.10	0.25	-0.28	-0.11	0.30	1.00						
Sb	0.09	-0.04	0.04	0.13	-0.06	-0.20	0.23	-0.05	-0.33	-0.30	1.00					
As	-0.48	-0.14	-0.11	-0.02	-0.12	-0.12	-0.07	0.47	-0.26	0.14	0.21	1.00				
Se	-0.53	0.13	-0.13	-0.11	0.22	0.11	0.03	0.04	0.21	-0.01	-0.14	0.36	1.00			
Pb	0.15	-0.04	0.06	0.09	-0.18	-0.39	-0.09	-0.15	-0.21	-0.15	0.31	-0.12	-0.27	1.00		
Cd	0.14	-0.03	-0.07	0.08	-0.05	0.07	0.16	-0.14	0.05	0.05	0.14	-0.10	-0.27	0.01	1.00	
Zn	0.00	-0.03	-0.02	0.16	-0.09	-0.19	0.08	-0.13	-0.23	-0.25	0.79	-0.08	-0.15	0.38	0.10	1.00

If the numerical value of the correlation coefficient between two variables x and y is fairly large, it implies that these two variables are highly correlated. In such cases it is feasible to try a linear relation of the form

$$Y = Ax + B$$

To correlate x and y, the constant A and B are to be determined by fitting the experimental data on the variables x and y to the equation. According to the method of least squares, the value of constants A and B are given by the relations

$$B = \bar{y} - Ax$$

$$\text{Where } \bar{x} = \frac{\sum x}{n} \quad \bar{y} = \frac{\sum y}{n} \quad A = n \frac{\sum (x * y) - \sum x * \sum y}{n \sum c - \bar{x}^2}$$

By using these relations with the help of microsoft excel finding the values of correlation coefficients (r) which has been given above Table 4. The strong positive correlation observed between EC and total hardness (0.88), sodium and conductivity (0.92), sodium and total hardness (0.75). Moderate correlation observed between sodium and potassium (0.60). High EC in the water is due to the high solubility of calcium and magnesium and high hardness is due electrical conductivity which depends on total dissolved solids. The moderate positive correlation observed between K⁺ and EC (0.52), DO and EC (0.51), DO and TH (0.54). The moderate positive correlation found between Cl⁻ and EC(0.54), Cl⁻ and Na⁺ (0.53), while negative correlation between Cl⁻ and SO₄²⁻ (-0.50). The negative correlation observed between SO₄²⁻ and EC (-0.51).The strong positive correlation observed between Zn and Sb (0.79). While negative correlation observed between As and pH (-0.48) and Se and pH (-0.53).

CONCLUSION

This study has been successfully demonstrated the utility of multivariate statistical tools including factor and cluster analysis to characterize the groundwater quality of Bacheli and Kirandul area. Factor analysis converted the twenty parameters in two factors which explained the data set with minimum loss of information. The first factor termed as salinization factor explained 33.479 % of the total variance and 33.479 % of cumulative. The second factor can be called as alkalinity factor, which explained 13.831 % of the total and 47.311 % of cumulative variance. Hierarchical cluster analysis grouped in twenty sampling station of city into three cluster. Cluster 1 (highly

polluted water) is more polluted than cluster 2 (Moderately polluted water) and than cluster 3 (relatively less polluted water). It provides great classification of the ground water quality of study are that can applied to the optimization of future spatial monitoring network with the lower cost.

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