EXCELLENT PUBLISHERS

International Journal of Current Research and Academic Review

ISSN: 2347-3215 Volume 3 Number 12 (December-2015) pp. 77-87

www.ijcrar.com

Hydrogeochemical Assessment of Ground water Sources of Kollam, India by Multivariate Statistical Approach

Nissy Anil John[1]* and Salom V Gnana Thanga[2]

[1]School of Energy, Earth & Environmental Sciences, Central University, Kerala, South India
[2]Department of Environmental Sciences, University of Kerala, Kariavattom, Thiruvananthapuram- 695581, Kerala, Inida

Corresponding author

KEYWORDS

Hydrochemistry, Ground water, Drinking water quality, Major ion chemistry, Physic-chemical characteristics

A B S T R A C T

The Multivariate statistical technniques Cluster Analysis (CA) and Factor Analysis (FA) was used to analyze the groundwater hydrochemical data of 35 samples for the monsoon and non- monsoon 2008 to extract the principal factors corresponding to the different sources of variation of hydrochemistry. The study was done with an objective of defining the main controls of hydrochemistry at the aquifer scale and to determinethe hydrochemical facies of dominant water types in the region. Chloride was found as dominating ion. Based on the chemical characteristics, three dominant groundwater types of Kollam, (Ca-Mg-HCO_3-Cl; Mg-Ca-HCO_3-Cl; and Ca-HCO_3-Cl), were observed with hydrochemical variations which may be attributed to mixed water or water exhibiting cyclic processes of dissolution, mixing and reverse ion exchange. Hydrochemical characteristics of groundwater in the region showed detrimental effect both qualitatively and quantitatively. Major deviations in chemical variation of hydrochemical facets of aquifer units in the study area imply that they behaved autonomously due to subsurface structural setting. This is attributed to the tertiary succession of Quilon formation which represents the sediments laid down in Kerala basin that existed during the Mio-pliocene times. The allied trends in its chemical alterations may be linked to the natural and anthropological causative features. The present study demonstrates the usefulness of multivariate statistical techniques in hydrochemistry.

Introduction

Water is vital and limiting resource to men and all living beings. Without proper management of water it is difficult to imagine its productive use for human activity be it agriculture or livestock. Therefore the quality of water is of utmost importance to quantity in any water supply planning. The quality of water may be influenced by natural and anthropogenic effects including local climate, geology and irrigation practices. It is a function of the physical, chemical and biological characteristics and could be subjective, since it depends on a particular intended use. It is the chemical character of groundwater that determines its quality and extent of utilization.

Multivariate statistical techniques, cluster analysis (CA) and factor analysis (FA),are frequently employed to characterize the quality of groundwater. They are effective means of manipulating, interpreting and representing data concerning groundwater pollutants and geochemistry. Mahknecht *et al.* (2003) and Farnham *et al.* (2003) used FA to study geochemical evolution of groundwater contamination. Love *et al.* (2004) applied FA to distinguish several groundwater signatures, including uncontaminated groundwater, agricultural and mining activities and sewage pollution. Suk and Lee (1999), Reghunath et al. (2002) and Kim *et al.* (2005) have used CA to interpret the hydrochemical data based on factor scores. The present study is an attempt to examine the quality of groundwater in Kollam (formerly known as Quilon), a coastal city in the South West of India. The data has been analyzed with reference to BIS and WHO, ionic relationships, hydrochemical facies and water types are identified based on different classification schemes. Multivariate statistical analyses viz., factor and cluster analysis are carried out to investigate the factors controlling ground water chemistry. Multivariate treatment of environmental data is successfully used to interpret relationship among the variables so that the environmental system could be better managed (Grandes et al. 1996; Gangopadhya et al. 2001). Factor and cluster analyses are also used to handle large water quality data sets and identify the dominant mechanism and factors which control ground water chemistry (Kim et al. 2005; Senthil Kumar et al. 2008).

Kerala state with a total area of 38,864 Km^2 has a groundwater potential of 5000 Mm^3. Several researchers have investigated the hydrochemical characteristics of ground water in different urban and semi-urban areas (Sarojini et al. 1997; Subramani et al. 2005; Umar et al. 2006; Pandian and Shankar 2007; Raju 2007). The municipal and industrial wastewater discharge constitutes the major polluting source while surface run-off is the seasonal phenomenon contributing to appreciable levels of pollution. The main objectives of this paper is to assess the chemistry of groundwater and to identify the geological and anthropological factors that presently affect the groundwater in the region using multivariate statistical techniques

Materials and Methods

Description of the study area

The study region Kollam (wards n=51) with an overall area (57 km^2) in Kerala lies between North latitudes 8˚ 50’ 15” and 80 56’ 35” and East longitudes 76˚ 32’17” and 76˚ 39’00. Climate has a major role in the hydrology and geomorphology of the region where the geological unit exposed belongs to the teritiary succession of Kerala known as Warkalli and Quilon formations of the Neogene (*Mio-Pliocene*) age (Padmalal et al. 1998). The study area is characterized by tropical humid climate with an oppressive summer, plentiful rainfall and temperature without wide variations during different seasons.

Sampling Sites and Chemical Analyses

Groundwater samples (n = 35) collected during both monsoon and non-monsoon during 2008 were analyzed to study the chemical variations. The samples were analysed for various physico - chemical parameters *viz*., temperature, pH, electrical conductivity (EC), total alkalinity (TA), salinity, total dissolved solids (TDS), total hardness (TH), nitrate (NO_3^-), phosphate (PO_4^{3-}), for cations (Ca^{2+}, Mg^{2+}, Na^+, K^+*)* and anions (HCO_3^-, CO_3^{2-}, SO_4^{3-}, Cl^-*)*. The temperature and pH were analyzed on site. Samples were carried in sterilized bottles and brought to the laboratory as early as possible to avoid any contamination. Physico-chemical analyses were performed following standard methods Trivedy and Goel (1984) and APHA (1992). The study area depicting the sampling stations is illustrated in Figure 1.

Statistical Analysis

Multivariate statistical analysis was done using Statistical Package for the Social Sciences (SPSS for Windows, v.17.0). Cluster analysis (CA) was used to determine the groups of samples with similar characteristics. The samples can be grouped statistically into distinct hydrochemical groups that may be significant in the geological context. The best dendrogram was obtained with the Euclidean distance. The Euclidean distance as similarity measurement together with Ward's method for linkage produces the most distinctive groups where each member within the group is more similar to its fellow members than to any member from outside the group.**)** Factor analysis was applied to determine the total number of factors for each data set in the analysis. Prior to the analysis, the data were standardized to produce a normal distribution of all variables (Davis 1973). Factor extraction was done with a minimum acceptable Eigen value as 1 (Kaiser 1958; Harman 1960). Orthogonal rotation of these initial factors to terminal factor solutions was done with Kaiser's varimax scheme (Kaiser 1960). This method maximizes the variance of the loadings on the factors and hence adjusts them to be either near ±1 or near zero (Davis 1973). Factor score coefficients are derived from the factor loadings. The value of each factor score represents the importance of a given factor at the sample site. A factor score (>+1) indicates intense influence by the process. Very negative values (< - 1) reflect areas virtually unaffected by the process while near - zero scores reflect areas with only moderate effect of the process.

Results and Discussion

Hydrochemistry of Groundwater

The descriptive statistics of groundwater samples during monsoon and non-monsoon is given in Table 1. The groundwater samples in the study area had TDS in a range 1.07 to 944 $mg.L^{-1}$ and were characterized by a pH ranged between 4.4 and 7.2. Among the cations, Na had the concentration ranging between 0.6 and 40 $mg.L^{-1}$.The order of abundance of major cations is $Ca^{2+}>Mg^{2+}>K^{+-}>Na^+$and that of anions is $Cl^->HCO_3^- SO_4^{3-}>NO_3^-$. The characteristics of groundwater with respect to anions revealed a relative abundance of Cl which varied 21.3 to 598.51 $mg.L^{-1}$during monsoon and non-monsoon of the study period.

Correlation coefficient is commonly used to measure and establish the relationship between two variables. It is a simplified statistical tool to show the degree of dependency of one variable to the other. The correlation matrix of 17 variables has been presented in Table 2 & 3. The correlation analysis of groundwater chemistry during monsoon showed that EC has strong positive correlation with Total Dissolved Solids (TDS), Salinity, Cl and Na indicating a common source. TDS showed strong positive correlation with salinity (r=1.00), Na (r=0.90) while total hardness showed significant positive correlation with Ca (r=0.82) and Mg. Salinity showed significant positive correlation with Na(r=0.90) and K. The high Na and Cl contents detected in certain samples may suggest the dissolution of chloride salts and indicative of the groundwater in the study area is brackish in nature. During non-monsoon TDS showed strong positive correlation withTH, Salinity(r=0.99) and calcium. Chloride showed significant positive correlation with SO4(r=0.83) and Ca.

The results of chemical analysis evaluated by cluster diagramsshow three main clusters. Cluster I consists of EC, TDS, salinity, Cl, TH & TAdesignate the brackish influence. Cluster II with Ca, SO_4, PO_4, NO_3, Na, Mg, K, pH and temperature indicate the source rock characteristics, anthropogenic pollution with sewage dumping, decaying and leaching, sanitary waste percolation while TC, FC & EC fall under cluster IIIpoint out the microbial contamination pathway towards the shallow groundwater aquifers through the alluvial sediments. The non-monsoon seasons also showed somewhat similar condition described earlier. Cluster II represents the anthropogenic pollution besides the brine dissolution during non-monsoon. Cluster III represents FC, TC shows affinity towards the brackish water,the source which might be attributed to the adjacent surface water (T-S canal) receiving enormous amount of sanitary wastes and sewages.It is also obvious that the shallow ground water aquifer facilitate the microbial pathogens to enter into the water source through the alluvial sediments in the study area.

Results of factor analysis of the groundwater chemistry data indicates six trends (factors) that can be related to various controlling processes presumed to have produced the different water species. During monsoon 2008 (Table 4),factor-1 is characterized by very high loadings of TDS, salinity, EC, Na, Cl, SO_4 and K indicating the brackish /saline water influence which contribute the TDS and leaching soluble constituents from source rock weathering. Weathering of silicates and carbonate minerals is a major source of Na and K. While Cl showed significant positive correlation with SO_4 (r =0.82). Factor-2 is associated with the high loadings of TH, Ca, and SO_4 & Cl. This factor can be ascribed to the trend of the dissolution of evaporitic minerals such as halite, gypsum and anthropogenic activities into the aquifer system. Carbonic acid weathering of silicate rocks can contribute to Ca, HCO_3, K, Mg, and Na. This factor reflects the signatures of natural water recharge and water-soil/ rock interaction (Olobaniyi and Owoyemi 2006).

During non-monsoon 2008, the first six factors constitute the representative factor model and constitute 74.082 % of variance. The factor-1 represents TH, EC, TDS, Ca, Na, SO_4; K and Cl indicate again the brackish water influence and the leaching of alkaline earth elements described earlier in the monsoon season is a unique grouping. Salinity showed high significant positive correlation with Na, K and Cl shows significant positive correlation with SO_4 (r =0.92). This chloride water type is widely reported within the coastal tract of Nigeria (Etu-Efeotor 1981; Udom et al. 1999). Factor 4 & 6 represents PO_4 and PO_4, K respectively indicating the percolation of land drainages. But factor-5 represents TA and Mg indicates the alkaline dominance contributed by runoff during monsoon and the plant debris. Source rock also induces the alkalinity to the groundwater reservoirs.

Figure 4 shows that Cl^- as dominating ion during the study period. The monsoon rains added high Cl^- to the shallow groundwater aquifers, which to a certain extent indicate organic pollution. The dominant water types of the region belong to belong to Ca-Mg-HCO_3-Cl; Mg-Ca-HCO_3-Cl; and Ca-HCO_3-Cl during both the seasons. Hence, it is evident that the samples have acquired their chemistry through rock-water/sediment interactions and dissolution mechanisms. Among the water types Ca-Mg-HCO_3-Cl; Mg-Ca-HCO_3-Cla are blended water which is inferior in quality compared to the fresh water types (Sahu and Sikdar, 2008) and consequently the water is slightly hard indicating the dominance of Chloride.

Table.1 Descriptive Statistics of Groundwater Samples

Parameters	Mean ± Standard deviation	
	monsoon	**non-monsoon**
Temperature	26.0 ± 0.7	26.8 ± 0.7
pH	6.9 ± 0.5	6.2 ± 0.4
EC	351 ± 221.6	352.60± 206.4
TDS	192± 190.4	271.8 ± 180.7
TA	260 ± 125.9	247.7 ± 181.2
TH	103 ± 47.9	124.3 ± 74.5
Salinity	132 ± 134.4	188.6 ± 126.5
Cl	126.9 ± 117	67.7 ± 22.95
SO_4	30.71 ± 9.9	24.2 ± 6.9
NO_3	0.86 ± 0.6	1.3 ± 1.1
PO_4	0.14 ± 0.1	0.06 ± 0.06
Ca	31.43 ± 17.1	34.8 ± 21.8
Mg	4.63 ± 5.9	9.4 ± 9.1
Na	3.40 ± 5.6	5.4 ± 8.8
K	6.20 ± 24.8	10.96 ± 14.4

(All units are expressed in mg/L except pH, EC (µS/cm);TH-Total Hardnes as CaCO3; TA-Total Alkalinity; TDS-Total Dissolved Solids)

Table.2 Correlation of Groundwater Samples During Monsoon

	TEMP	PH	EC	TDS	TA	TH	SAL.	CL	SO4	NO3	PO4	CA	MG	NA	K	TC	FC
TEMP	1																
PH	0.156	1															
EC	0.022	0.046	1														
TDS	0.3	0.177	**.512(**)**	1													
TA	0.054	0.027	**.343(*)**	-0.034	1												
TH	-0.006	0.001	0.165	0.009	**.367(*)**	1											
SAL.	0.304	0.182	**.504(**)**	**1.000(**)**	-0.04	0.004	1										
CL	0.067	0.116	**.521(**)**	**.366(*)**	0.152	**.401(*)**	**.363(*)**	1									
SO4	0.284	0.07	**.403(*)**	0.269	0.095	0.318	0.266	**.829(**)**	1								
NO3	-0.163	**-.335(*)**	-0.21	0.029	-0.247	0.126	0.023	0.007	-0.022	1							
PO4	-0.27	0.048	**.345(*)**	0.307	-0.156	-0.101	0.304	0.317	0.222	0.175	1						
CA	0.096	-0.076	0.211	-0.09	0.199	**.820(**)**	-0.097	**.341(*)**	0.31	0.014	-0.155	1					
MG	-0.053	-0.052	-0.029	0.127	0.216	**.550(**)**	0.129	0.272	0.185	0.14	0.024	0.096	1				
NA	**.381(*)**	0.297	**.465(**)**	**.908(**)**	-0.003	0.04	**.909(**)**	**.396(*)**	**.366(*)**	-0.104	0.263	-0.06	0.163	1			
K	0.165	0.1	0.322	**.481(**)**	-0.203	-0.111	**.479(**)**	**.427(*)**	**.359(*)**	0.237	0.142	-0.047	-0.127	**.502(**)**	1		
TC	-0.043	0.082	0.086	0.271	0.051	-0.153	0.275	-0.064	-0.164	-0.191	0.038	-0.174	-0.022	0.207	-0.081	1	
FC	-0.049	0.068	0.098	0.289	0.062	-0.153	0.292	-0.06	-0.16	-0.175	0.055	-0.182	-0.025	0.221	-0.074	**.994(**)**	1

*** Correlation is significant at the 0.05 level (2-tailed).**

**** Correlation is significant at the 0.01 level (2-tailed).**

Table.3 Correlation of Groundwater Samples During Non-monsoon

	TEMP	PH	COND	TDS	TA	TH	SAL.	CL	SO4	NO3	PO4	CA	MG	NA	K	TC	FC
TEMP	1																
PH	-0.002	1															
COND	0.144	0.03	1														
TDS	0.082	0.232	**.381(*)**	1													
TA	-0.108	0.317	0.173	0.32	1												
TH	-0.098	0.281	0.199	**.480(**)**	**.815(**)**	1											
SAL.	0.07	0.234	**.388(*)**	**.994(**)**	0.32	**.473(**)**	1										
CL	0.147	-0.043	0.144	0.256	0.226	**.389(*)**	0.259	1									
SO4	0.118	-0.074	0.072	0.256	0.087	0.174	0.259	**.836(**)**	1								
NO3	-0.061	0.124	0.058	0.168	**.378(*)**	**.396(*)**	0.143	**.369(*)**	0.208	1							
PO4	0.203	-0.143	0.261	0.019	0.011	0.001	0.02	0.061	0.097	0.037	1						
CA	-0.097	0.272	0.096	**.493(**)**	**.630(**)**	**.878(**)**	**.479(**)**	**.497(**)**	0.31	**.372(*)**	-0.124	1					
MG	-0.095	0.171	0.302	0.26	**.727(**)**	**.731(**)**	0.268	0.038	-0.122	0.286	0.168	0.326	1				
NA	0.189	**-.445(**)**	0.331	0.164	-0.093	-0.014	0.178	0.071	0.02	0.11	0.285	0.016	-0.047	1			
K	-0.102	0.06	0.298	0.165	0.254	0.169	0.17	0.141	0.183	0.114	**.523(**)**	0.072	0.28	-0.072	1		
TC	0.175	-0.268	-0.157	-0.167	0.172	0.116	-0.164	-0.166	-0.284	0.073	-0.029	-0.017	0.245	-0.038	-0.159	1	
FC	0.316	-0.019	-0.097	-0.088	0.196	0.159	-0.085	-0.104	-0.215	0.198	0.024	0.083	0.188	0.026	-0.147	**.772(**)**	1

**** Correlation is significant at the 0.01 level (2-tailed).**

*** Correlation is significant at the 0.05 level (2-tailed).**

Table.4 Varimax Rotated Factor Loading Matrix for Groundwater Samples

Variables	F1	F2	F3	F4	F5	F6
Temperature	0.322	0.011	0.002	-0.679	**0.402**	0.162
Mg	0.192	0.386	0.261	0.361	**0.431**	-0.528
pH	0.255	-0.148	0.129	-0.449	-0.165	-0.509
Ca	0.111	**0.73**	0.289	-0.028	0.069	0.373
K	**0.581**	-0.038	-0.511	-0.07	0.019	0.262
PO_4	0.379	-0.102	-0.289	**0.505**	-0.445	-0.254
FC	0.225	-0.626	**0.599**	0.287	0.039	0.228
TC	0.212	-0.623	**0.607**	0.272	0.04	0.225
EC	**0.679**	0.13	0.137	0.044	-0.464	0.163
NO_3	-0.052	0.158	-0.496	**0.557**	**0.417**	0.147
Na	**0.893**	-0.205	-0.038	-0.125	0.193	-0.132
SO_4	**0.602**	**0.496**	-0.112	-0.088	-0.199	0.103
TA	0.098	0.318	**0.607**	-0.099	-0.17	-0.088
Salinity	**0.888**	-0.282	-0.058	0.028	0.225	-0.048
Cl	**0.69**	**0.479**	-0.031	0.115	-0.263	0.044
TDS	**0.889**	-0.275	-0.059	0.033	0.221	-0.042
TH	0.194	**0.784**	0.394	0.175	0.25	-0.026
Eigen value	4.522	2.928	2.051	1.601	1.307	1.03
% variance	26.6	17.224	12.064	9.42	7.688	6.058
Cum %	**26.6**	**43.824**	**55.888**	**65.308**	**72.996**	**79.054**

EC - Electrical Conductivity; TH - Total Hardness; TA - Total Alkalinity; TDS - Total Dissolved Solids, TC – Total coliforms, FC – Fecal coliforms

Figure.1 Map Showing Water Sampling Stations in Kollam

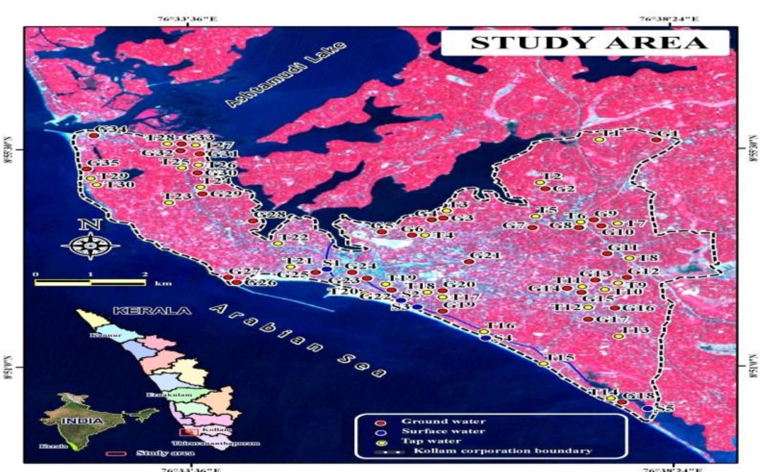


Fig.2and 3 Dendrogram of Hydrochemical Samples during Monsoon and Non-monsoon

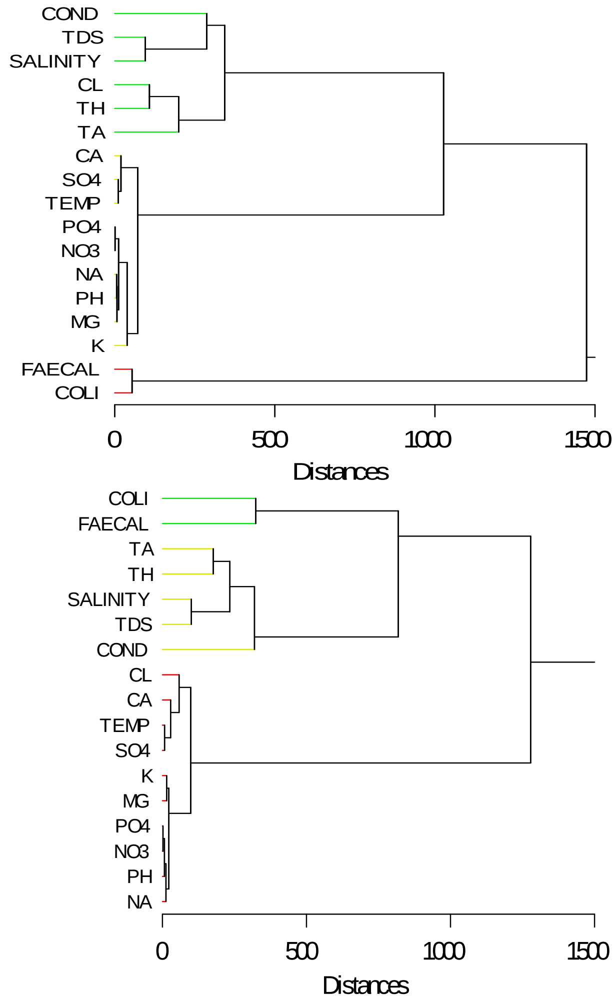
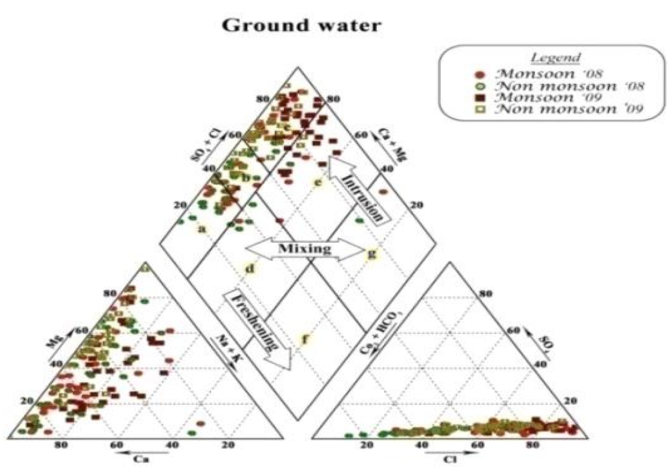


Fig.4 Piper Trilinear Diagram for Groundwater Samples



Conclusion

Multivariate statistical method used in this study (Pearson correlation coefficients) help to find statistically important factors in data variability and thus improve conclusions in environmental impact studies. Pearson correlation matrix was applied toall the collected water samples for identifying the possible statistical relationship between different pairs of ground water quality parameters.

In the present study, apart from water quality assessment, pattern recognition techniques were used to study the chemistry of groundwater. Based on the study, the ground water characteristics with different chemical groups were identified to dominate in the study area. The chemical signature attained may be explained through rock-water/sediment interaction, dissolution, mixing and reverse ion exchange during both monsoon and non-monsoon seasons. The main processes controlling the hydrochemistry of the groundwater in the water sources of Kollam are mixing and dissolution reactions, respectively and the dominant percentage of groundwater samples of Kollam region is normal earth alkaline origin which belongs to Ca-Mg-HCO3-Cl; Mg-Ca-HCO3-Cl and Ca-HCO3-Cl. The ground water in Kollam is dominated by water types characterized as blended water. The study reveals that there is remarkably immense anthropogenic influence up to the level of shallow aquifers and the contact with the brines. Unscrupulous chemical input from the sewages and industries have largely affected the hydrochemical characteristics of ground water. Much of the quality parameters are influenced by the weathering of silicate minerals and dissolution of evaporitic minerals from the source rocks and leaching of soils. The transitional water types may be attributed to the formation of quaternary aquifers (Warkalli aquifers) apart from anthropogenic influences.

References

APHA. (1992). Standard Methods for the Examination of Water and Waste Waters, American Public Health Association, 18th Edition Washington, DC.

Davis J.C (2002) Statistics and data analysis in geology. Wiley, New York.

Farnham, I. M., Johannesson, K. H., Singh, A. K., Hodge, V. F. and Stetzenbach, K. J. (2003). Factor analytical approaches for evaluating groundwater trace element chemistry data. Analytica Chimica Acta, 490 (1-2), 123-138.

Grande, J.A., Borrego, J., Torre, M.L. and Sainz, A. (2003) Application of cluster analysis to the geoche-mistry zonation of the estuary waters in the tinto and odiel rivers (Huelva, Spain). Environmental Geochemistry and Health, 25: 233-246.

Kaiser, H. F. (1960). The application of electronic computers to factor analysis.Educational and PsychologicalMeasurement, 20, 141-151.

Kim, J. H., Kim, R. H., Lee, J. H., Cheong, T. J., Yum B. W. and Chang, H. W. (2005). Multivariate statistical analysis to identify the major factors governing groundwater quality in the coastal area of Kimje, South Korea. Hydrological Processes, 19 (6), 1261-1276.

Love, D., Hallbauer, D., Amos, A. and Hranova, R. (2004) Factor analysis as a tool in groundwater quality management: two southern African case studies. Physics and Chemistry of the Earth, 29 (15-18), 1135-1143.

Mahlknecht, J., Steinich, B. and Navarro de Leon, I. (2003). Groundwater chemistry and mass transfers in the Independence aquifer, central Mexico, by using multivariate statistics and mass-balance models.

Olobaniyi SE, Owoyemi FB (2006) Characterization by factor analysis of the chemical facies of groundwater in the Deltaic Plain Sands aquifer of Warri, Western Niger Delta. UNESCO/ African journal of Science and Technology: Science and Engineering Series 7(1):73–81.

Padmalal, D., Shaji, B. R and Baji R. (1995). Sedimentological studies of the tertiary deposited at Pozhikkara, Kerala- its environmental significance. Proceedings of 7th Kerala Science Congress. pp 275-277.

Reghunath, R., Murthy, T. R. S. and Raghavan, B. R. (2002). The utility of multivariate statistical techniques in Hydrogeochemical studies: an example from Karnataka, India. Water Research, 36 (10), 2437-2442.

Sahu, P., and Sikdar, P.K. 2008. Hydrochemical framework of the aquifer in and around East Kolkata wetlands, West Bengal. India Environmental Geology, 55: 823-835

Sarojoni, G., M, Singanam, K.S.Rao, M., Sarath Babu, and A. Ratnakar.1997. Monitoring the status of Kollera areas villages' water resources. Indian Journal of Environmental Protection. 17(7):481-484.

Subramani, T., Elango, L., and Damodarasamy, S.R. (2005). Groundwater quality and its suitability for drinking and agricultural use in Chithar River Basin, Tamil Nadu, India. Environ. Geology. 47: 1099–1110.

Suk, H.J. and Lee, K.K. (1999). Characterization of a ground water hydrochemical system through multivariate analysis: clustering into ground water zones. Ground Water, 37(3), 358-366.

Trivedy, R.K., and Goel, P.K. (1984). Chemical and biological methods for water pollution studies. Environmental Publications, Karad, India.

Umar, R., Muqtada, M., Khan, A and Absar, A. (2006). Groundwater hydrochemistry of a sugarcane cultivation belt in parts of Muzaffarnagar district, Uttar Pradesh, India. Environmental Geology. 49: p. 999-1008.