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Full Length Research Paper

Seasonal variations in groundwater quality: A statistical approach

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In this study, a descriptive statistical measure and a partial correlation analysis were applied to groundwater quality data set monitored in pre-monsoon and post-monsoon for three years to investigate seasonal variations of Central Ganga Plain in India. The variables were divided into two categories as "chemical property- HCO_3, Cl, SO_4, Na, K, Ca, and Mg" and "physical property- electrical conductivity (EC), pH and hardness". The results revealed that groundwater quality variables (chemical property and physical property) were distinctly different between two seasons. Seasonal changes of groundwater quality caused by ion exchange, dissolution mechanism and anthropogenic influences such as fertilizer, pesticides, agricultural activities, and other industrial units should be taken into consideration by the groundwater managers especially in post monsoon 2005 seasons in which higher concentrations were observed. From the partial correlation coefficient analysis of groundwater samples, dominance of alkalis and relative abundance of SO_4 during post monsoon were inferred. In the case of the groundwater samples, strong correlation were observed among HCO_3 with Cl, SO_4, Na, Ca, pH and hardness in the post-monsoon (2005) samples, as well as negative correlation were found among the major variables except HCO_3 with Na, Mg, hardness during the pre-monsoon (2006) suggested from partial correlation of groundwater samples.

Key words: Seasonal variation, groundwater quality, descriptive statistical measures, partial correlation analysis.

INTRODUCTION

In Central Ganga Plain (CGP), agricultural activities, increased use of fertilizers, pesticides, population growth, rapid industrialization, unplanned urbanization and the failure of monsoon and improper management of rain water in the Ganga Plain have resulted in various geo-environmental hazards causing deterioration of groundwater quality in many ways. Therefore, it is necessary to monitor and evaluate water quality on regular basis. In India, almost 80% of the rural population depends on untreated ground water supplies (Reza et al., 2009) and it is generally considered that the groundwater is least polluted compared to other inland water resources, but studies indicated that groundwater is not absolutely free from pollution, though it is likely to be free from suspended solids. The major problem with the groundwater is that, once contaminated, it is difficult to restore its quality. Hence, there is a need and concern for the protection and management of groundwater quality (Gajendaran and Thamarai, 2008).

Groundwater quality in an area is a function of physical and chemical parameters that are greatly influenced by

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geological formations and anthropogenic activities (Subramani et al., 2005). Water quality monitoring has one of the eminent priorities in environmental protection policy (Simeonov et al., 2002). The particular problem in water quality monitoring is the complexity associated with analyzing large number of measured variables (Saffran, 2001). The chemical composition of groundwater is controlled by many factors that include the precipitation, mineralogy, climate and topography. These factors can combine to create diverse water types that change in composition spatially and temporally (Chenini and Khemir, 2009). Understanding the quality of groundwater with its temporal and seasonal variation is important because it is the factor that determines the suitability for drinking, domestic, agricultural and industrial purposes (Amadi and Olasehinde, 2008; Amadi et al., 2010).

The assessment of environmental quality is mostly based on vast amounts of physical, chemical, and biological data, which if processed using descriptive univariate methods, is of little value to decision makers. Simple assessments can be made using descriptive statistics and some graphical representations. Many research have been carried out on statistical analysis to assess the groundwater quality (Aravinda, 1991; Singanan and Rao, 1995; Srivastava and Sinha, 1994; Ratha and Venkataraman, 1997; Biswal et al., 2001; Keshavan and Parameshwari, 2005; Prajapati and Mathur, 2005; Patowary and Bhattacharya, 2005; Mahajan et al., 2005; Gajendaran and Thamarai, 2008; Pathak et al., 2008; Karunakaran et al., 2009). In particular, Spanos et al. (2003) adopted multivariate statistical approaches in deriving hidden information from the data set about the possible influences of the environment on water quality. Statistical investigation offered more attractive options in environment science, though the results may deviate from real situations (Nemade and Shirivastava, 2004; Gajendaran and Thamarai, 2008).

Surface water, groundwater quality assessment and environmental research employing multi-component techniques are well described in the literature (Praus, 2005). Descriptive statistical methods including factor analysis were used successfully in hydrochemistry for many years. Ratha and others (1993), Henburg and Bruemer (1993) and Cambier (1994) used statistical methods, such as, multivariate analysis, to find the correlation between physical variables and chemical variables. However, the literatures are available on the study of seasonal variations in surface water quality measured by different statistical analysis but a few researchers who focused on groundwater quality assessment using statistical methods. Thus, in this study, a descriptive statistical measures and a partial coefficient analysis both were carried out to establish seasonal variations in the concentration levels of groundwater samples as well as to see the relationship among the chemical and physical variables on the pre-monsoon and post-monsoon periods.

MATERIALS AND METHODS

Study area

The selected study area is lying between rivers Hindon and Krishni with area of 650 km^2 (29°05'N-29°30'N: 77°20'E-77°32'E) located in the western part of Muzaffarnagar district in the state of Uttar Pradesh, India (Figure 1). Sugarcane is the principal crop of the area. Groundwater is the major source of potable, agriculture, industrial and other usage.

The area on an average, receives an annual rainfall of 588 to 697 mm, as recorded by two raingauge stations. Rainfall is the main source for the recharge of the groundwater system. Drainage is controlled by the two north to south flowing rivers and elevation varies between 224 and 256 m above sea level (Khan, 2009).

Geologically, the area is underlain by alluvial deposits of Quaternary age consisting of older and younger alluviums. The thickness of the alluvium in the area is approximately 1.3 km (Singh, 2004; Kumar, 2005; Umar et al., 2006). The subsurface data available from shallow boreholes (Figure 2) indicate that the top clay layer is persistent throughout the area and is underlain by a more porous and thicker granular zone intervened by several clay lenses. The aquifer tends to behave as a monostratum to depth of about 120 m (Khan et al., 2010). The granular zone is composed of medium to coarse sand and gravel and form about 60 to 75% of the total formation encountered particularly in the upper central part of the study area. This area being a down faulted area due to NE-SW Muzaffarnagar fault possibly became a dominant recipient of sand than the north area of the fault. Muzaffarnagar fault is an active transverse E-W fault passing through the river courses of Yamuna, Krishni, Hindon, Kali and city of Muzaffarnagar (Umar et al., 2009; Bhosle et al., 2007).

Methods

Groundwater samples were collected from representative sampling stations established over the entire study area, for chemical analysis in November 2005, June 2006 and June 2007; from 38 locations representing post- and pre-monsoon periods, respectively. The depth of sampled hand pumps is 12-72 m bgl. Ten parameters such as, pH, EC, hardness, HCO_3 , Cl, SO_4, Na, K, Ca, and Mg were selected as the groundwater quality variables for analyses. The water samples were analysed as per the standard methods of APHA (1992). Values of pH were measured by a portable digital water analyses kit with electrodes. The instrument was calibrated with buffer solutions having pH values of 4 and 9. Total dissolved solids (TDS) were calculated by summing up the concentrations of all the major cations and anions. The values of EC were measured by portable kit with electrodes in the lab. The concentrations of Ca^{++}, Mg^{++}, Cl^-, HCO_3^- and total hardness were determined by volumetric method. Ca^{++} and Mg^{++} were determined by EDTA titration. For HCO_3^-, HCl titration to a methyl orange point was used. Chloride was determined by titration with $AgNO_3$ solution. Flame emission photometry was used for the determination of Na^+ and K^+. Sulphate was determined by gravimetric method.

Prior to the statistical analysis, all the chemical data were normalized by log (C/1-C) for major elements, where C is the weight fraction of the elements (Ratha and Sahu, 1993a, 1994). This transformation was followed because it eliminates discreetness as well as closure effects and makes the joint distribution of chemical constituent's multivariate normal, so that proper geochemical inferences are possible. Again, usually the results of chemical

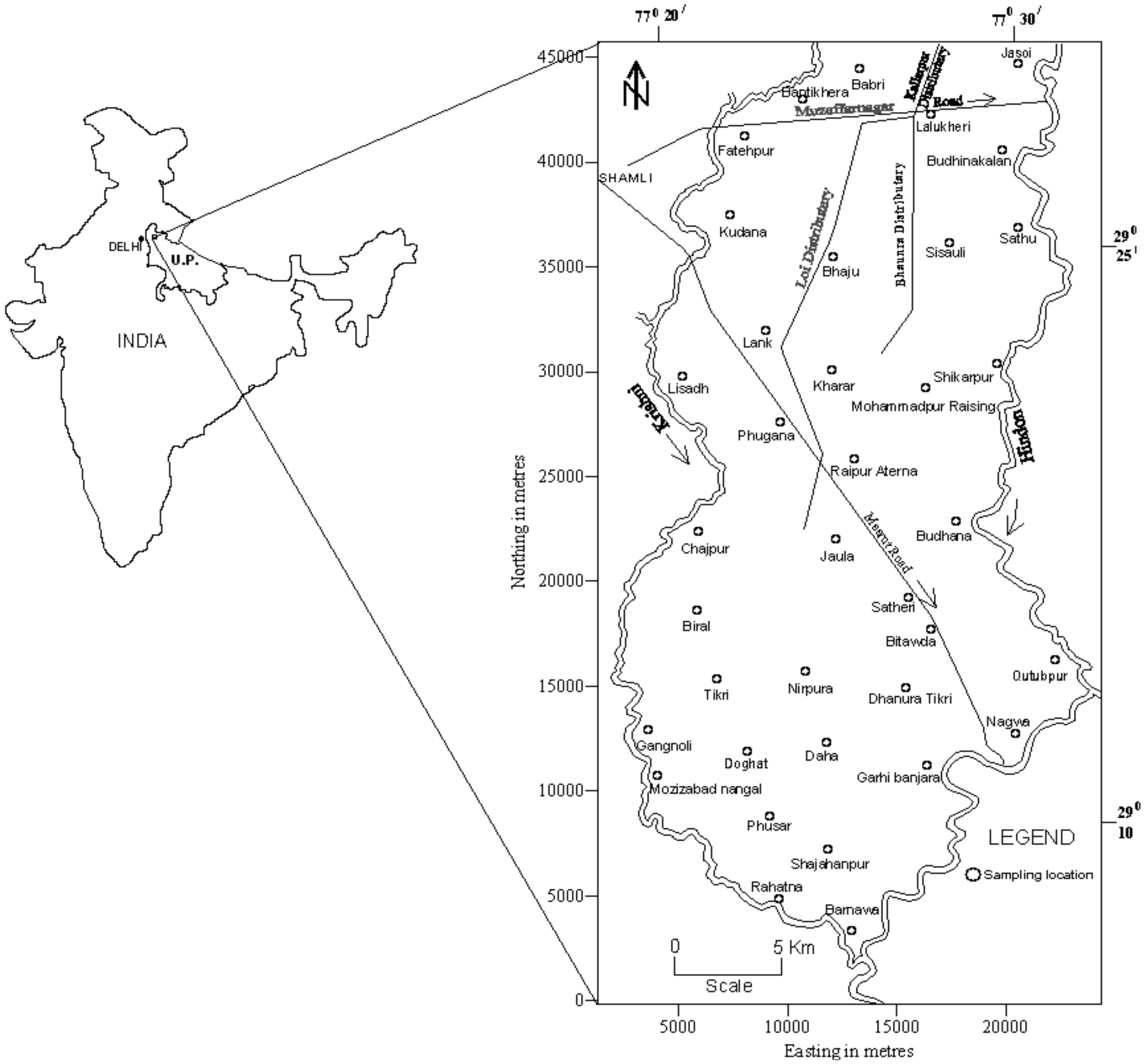

Figure 1. Location map of the study area.

analysis are expressed in fractions or percentage totaling 1 or 100 (that is, fixed sum), which induces artificial negative associations of different degrees among the constituents, which must be removed to obtain true associations for any inferences. This negative association can be avoided for all types of components by using log (C/1-C) transformation. This transformation normalizes the distribution (Ratha and Sahu, 1993a, 1994) of major elements and other chemical components in groundwater.

The statistical analysis of groundwater samples of the study area provide us an opportunity to study and the seasonal variation in the concentration through statistical analyses and to relate them with various natural and anthropogenic causes reported in the study area. Prior to this application, Ratha and others (1992), Ratha and Sahu (1993a, 1993b), Ratha and others (1994b) and Ratha and Sahu (1994) have used discriminant statistical analysis to establish the anthropogenic contribution of contaminants in groundwater due to agricultural and industrial activities. It is to be noted that only ten variables such as pH, conductivity, hardness, HCO_3, Cl, SO_4, Na, K, Ca, and Mg, which are common to both the seasons are considered for discriminant statistical analysis. Descriptive statistical analysis was used in this study to calculate the mean, standard deviation and standard error by using software SPSS of all the variables of groundwater. The partial correlation coefficient (*r*), measures the strength of the relationship between the dependent variable and a single predictor variable when the effects of the other predictor variables in the model are held constant (Anderson, 1984; Cooley and Lohnes, 1971).

RESULTS AND DISCUSSION

Descriptive statistical measures

The results of descriptive statistics (mean, standard deviation, standard error) of each data set are displayed in Tables 1, 2 and 3. Water samples analyzed for pH EC, hardness, HCO_3, Cl, SO_4, Na, K, Ca, Mg in groundwater samples for 3 years (2005–2007) in pre-monsoon and

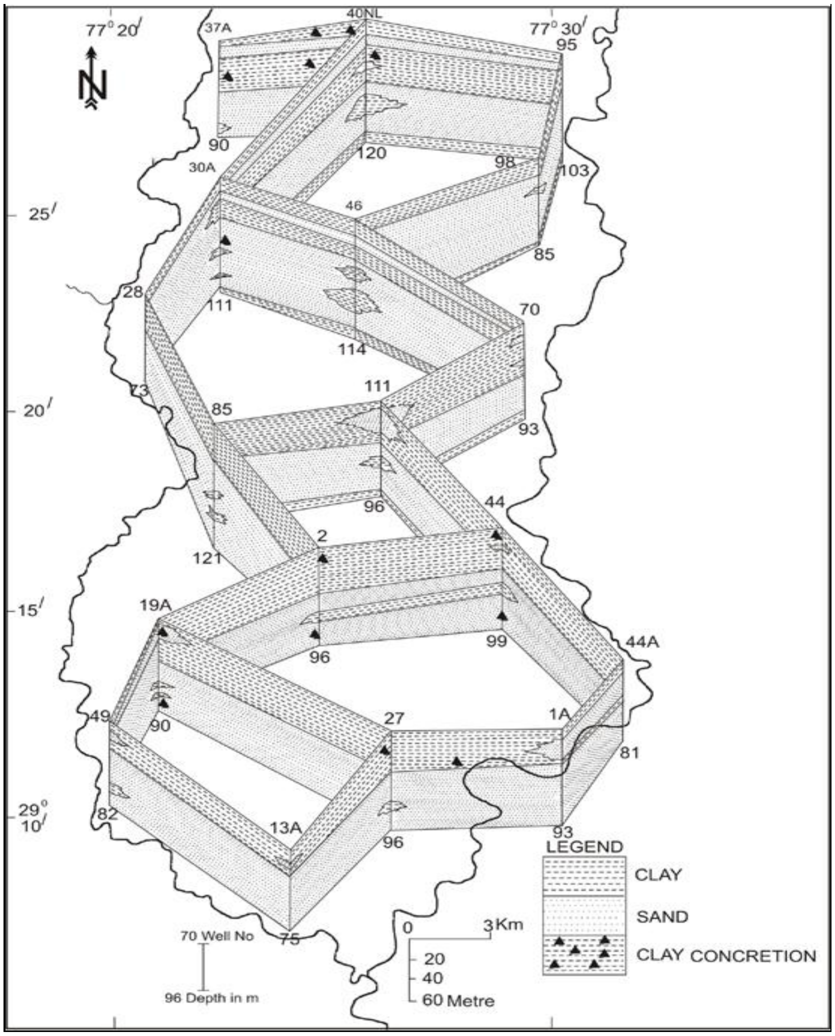

Figure 2. Fence diagram.

Table 1. Summary of chemical parameters of groundwater samples with the result of test of significance difference in mean (post-monsoon 2005 and pre-monsoon 2006).

Variables	Groundwater post-monsoon (2005)		Groundwater pre-monsoon (2006)		Standard error (SE)	m_1-m_2	m_1-m_2/SE
	Mean (m_1)	Standard deviation	Mean (m_2)	Standard deviation			
pH	8.103	0.323	8.019	0.350	0.040	0.084	2.126
EC	448.649	175.787	435.136	115.990	17.330	13.514	0.780
Hardness	288.566	108.581	180.865	83.677	12.891	107.703	8.355
HCO_3	0.156	0.104	0.142	0.098	0.012	0.015	1.295
Cl	1.383	0.340	1.343	0.361	0.041	0.040	0.975
SO_4	0.864	0.332	0.663	0.275	0.0373	0.200	5.389
Na	0.762	0.224	0.577	0.097	0.0228	0.185	8.153
K	2.020	0.264	2.093	0.276	0.032	-0.073	-2.321
Ca	1.252	0.288	1.970	0.355	0.057	-0.718	-12.797
Mg	1.552	0.319	1.449	0.205	0.032	0.103	3.247

pH, −log10H^+, EC (in μS/cm) at 25°C.
Note: all samples are from hand pump.

Table 2. Summary of chemical parameters of groundwater samples with the result of test of significance difference in mean (post-monsoon 2005 and pre-monsoon 2007).

Variables	Groundwater post-monsoon (2005)		Groundwater pre-monsoon (2007)		Standard error (SE)	m_1-m_3	m_1-m_3/SE
	Mean (m_1)	Standard deviation	Mean (m_3)	Standard deviation			
Ph	8.103	0.323	8.019	0.350	0.403	0.084	0.208
EC	448.649	175.787	470.271	110.215	30.550	-21.622	-0.708
Hardness	288.568	108.581	234.190	77.253	19.860	54.378	2.738
HCO_3	0.157	0.104	0.122	0.072	0.050	0.035	0.691
Cl	1.383	0.340	1.365	0.314	0.0430	0.018	0.411
SO_4	0.864	0.332	0.700	0.215	0.0351	0.163	4.660
Na	0.762	0.224	0.712	0.124	0.0261	0.050	1.916
K	2.020	0.264	1.935	0.188	0.0623	0.085	1.364
Ca	1.252	0.288	1.780	0.273	0.047	-0.528	-11.352
Mg	1.552	0.319	1.317	0.204	0.0467	0.235	5.229

pH −log10H^+; EC, electrical conductivity (in μS/cm) at 25°C.
Note: all samples are from hand pump.

Table 3. Summary of chemical parameters of groundwater samples with the result of test of significance difference in mean (pre-monsoon 2006 and pre-monsoon 2007).

Variables	Groundwater pre-monsoon (2006)		Groundwater pre-monsoon (2007)		Standard error (SE)	m_2-m_3	m_2-m_3/SE
	Mean (m_2)	Standard deviation	Mean (m_3)	Standard deviation			
Ph	8.019	0.350	8.019	0.350	0.041	-0.000	-0.000
EC	435.136	115.990	470.271	110.215	13.310	-35.135	-2.640
Hardness	180.865	83.677	234.190	77.253	9.861	-53.324	-5.408
HCO_3	0.142	0.0976	0.122	0.072	0.011	0.020	1.959
Cl	1.343	0.361	1.367	0.314	0.040	-0.022	-0.563
SO_4	0.663	0.275	0.700	0.215	0.029	-0.037	-1.294
Na	0.577	0.097	0.712	0.124	0.016	-0.135	-8.968
K	2.093	0.276	1.935	0.188	0.029	0.158	5.480
Ca	1.970	0.355	1.800	0.273	0.039	0.190	4.942
Mg	1.449	0.205	1.317	0.204	0.025	0.133	5.322

pH −log10H^+; EC, electrical conductivity (in μS/cm) at 25°C.
Note: all samples are from hand pump.

post-monsoon were subjected to descriptive statistical measures. The reason for examining variations comparing two periods (pre-monsoon and post-monsoon seasons) was the considerable differences in climatic and hydrological conditions respectively, of the region leading to water quality changes. In this study, the variables were divided into two categories such as physical property (pH, EC and hardness) and chemical property like cation (HCO_3, Cl, SO_4) and anion (Na, K, Ca, Mg) respectively, to investigate seasonal variations of groundwater quality. Mean values of chemical properties both anion and cation which are not affected by extreme values were taken into consideration as characteristics values to see the differences in the two different seasons (see Table 1, 2 and 3). Comparing the mean values in Table 1 and 2, it can be concluded that Cl, K, and Ca were slightly higher and HCO_3, SO_4, and Na were lower in the groundwater pre-monsoon periods 2006 and 2007 than in the post-monsoon period 2005. On the other hand, the mean value of physical properties (pH and hardness) were clearly lower in the pre-monsoon in 2006 and 2007 compared to post monsoon period in 2005, and showed a clear-cut temporal effect. But from the Table 3, it was observed that chemical concentration of HCO_3, SO_4, Cl

Table 4. Partial and Pearson correlation coefficient for groundwater samples (post-monsoon 2005).

	Partial correlation coefficient for groundwater samples									
	HCO_3	**Cl**	**SO_4**	**Na**	**K**	**Ca**	**Mg**	**EC**	**pH**	**HARD**
HCO_3	1.000									
Cl	0.095	1 .000								
SO_4	0.157	-0.507	1.000							
Na	0.136	0.232	-0.521	1.000						
K	-0.282	-0.117	-0.435	0.507	1.000					
Ca	0.150	-0.115	0.0314	-0.591	-0.238	1.000				
Mg	-0.549	-0.165	0307	-0.264	-0.324	-0.345	1.000			
EC	-0.059	-0.402	0.377	-0.502	-0.397	0.377	0.226	1.000		
pH	0.112	0.426	-0.474	0.016	0.027	0.189	-0.078	-0.127	1.000	
HARD	0.461	-0.055	0.027	0.326	0.007	0.082	-0.457	0.173	-0.155	1.000
	Pearson correlation coefficient for groundwater samples									
HCO_3	1.00									
Cl	0.444**	1.000								
SO_4	0.388*	0.265	1.000							
Na	0.079	0.051	-0.473**	.000						
K	0.068	0.431**	0.042	0.364*	1.000					
Ca	0.200	0.063	0.111	-0.594**	-0.108	1.000				
Mg	-0.289	0.209	0.224	-0.276	-0.049	-0.269	1.000			
EC	-0.222	-0.512**	0.072	-0.433**	-0.513**	0.292	0.069	1.000		
pH	0.124	0.274	-0.354*	0.011	0.053	0.194	-0.054	-0.135	1.000	
HARD	0.091	-0.475**	-0.291	0.320	-0.302	-0.011	-0.547**	0.333*	-0.159	1.000

pH −log10H^+; EC, electrical conductivity (in µS/cm) at 25°C; HARD, hardness of all samples from hand pump.
**Correlation is significant at 0.01 level; *correlation is significant at 0.05 level.

and Na were slightly higher and K, Ca and Mg were lower in groundwater pre-monsoon period in 2007 than in the pre-monsoon period in 2006. On the other hand, the mean values of physical properties pH, EC and hardness were clearly higher in the pre-monsoon in 2007 compared to pre-monsoon period in 2006. Prior to the partial correlation coefficient, a test of significance in the difference in mean (Mode 1958; Rickmers and Todd, 1967) of different variables of both the seasons were carried out to guide in the selection of effective variables for partial correlation analysis. It was also observed that in the case of groundwater samples (Tables 1, 2 and 3), almost all the variables show significant difference in the mean, except pH and Cl.

Comparing the standard deviations values in Tables 1, 2 and 3, it can be concluded that HCO_3 is more consistent and varied less from the mean concentration of chemical properties on groundwater and Cl and Ca both showed more variation from the mean concentration among the chemical properties. Again, in comparisons with the overall within the different pre- and post-monsoon periods, it was found that Na and HCO_3 are more consistent having less variation from standard deviation values (0.09613 and 0.07185) in the pre-monsoon periods 2006 and 2007 respectively.

Measurement of spearman correlation and partial correlation

The correlation coefficients (r) among various water quality parameters were calculated and the values of the correlation coefficients (r) are given in Tables 4, 5 and 6. The advantage of partial correlation over multiple correlations is that the latter often does not exhibit the exact correlation between the random variables. Also, partial correlation will give better geochemical interpretation with respect to seasonal variation in the data, that is, whether they are from pre-monsoon samples or from post-monsoon samples.

In the present case, partial correlation coefficient analyses of pre- and post-monsoon groundwater populations were carried out using physical and chemical parameters. For partial correlation analysis, all the variables of groundwater were considered. The results of partial correlation are presented in Tables 4, 5 and 6. In the case of post-monsoon groundwater samples in 2005, strong negative correlation were found between SO_4 and Cl, Ca and Na, Mg and HCO_3, Na and SO_4, and with EC and Na; whereas, in pre-monsoon 2006, strong negative correlation were found between Na and SO_4, Ca and K and with EC and K. Strong negative correlation were also

Table 5. Partial and Pearson correlation coefficient for groundwater samples (pre-monsoon 2006).

	HCO_3	Cl	SO_4	Na	K	Ca	Mg	EC	pH	HARD
Partial correlation coefficient for groundwater samples										
HCO_3	1.000									
Cl	-0.186	1.000								
SO_4	-0.176	-0.412	1.000							
Na	0.138	0.183	-0.580	1.000						
K	-0.082	-0.029	-0.104	0.269	1.000					
Ca	-0.015	-0.499	-0.085	-0.095	-0.514	1.000				
Mg	0.084	-0.182	-0.084	-0.239	-0.462	0.0723	0.000			
EC	-0.063	-0.441	0.306	-0.387	-0.504	0.574	0.274	0.000		
pH	-0.176	-0.130	0.180	-0.102	0.144	-0.025	-0.064	-0.077	1.000	
HARD	-0.498	-0.154	0.397	0.433	0.023	0.312	0.074	0.219	0.204	1.000
Pearson correlation coefficient for groundwater samples										
HCO_3	1.000									
Cl	-0.229	1.000								
SO_4	-0.215	-0.060	1.000							
Na	0.188	-0.192	-0.667**	1.000						
K	-0.127	0.207	0.073	0.000	1.000					
Ca	-0.089	-0.002	0.169	-0.369*	-0.172	1.000				
Mg	0.009	0.144	0.125	-0.428**	-0.196	0.315	1.000			
EC	-0.054	-0.389*	0.254	-0.295	-0.485**	0.441**	0.215	1.000		
pH	-0.178	-0.086	0.176	-0.103	0.144	-0.002	-0.040	-0.079	1.000	
HARD	0.414*	-0.611**	-0.299	0.556**	-0.143	-0.002	-0.135	0.222	0.171	1.000

pH, $-\log 10H^+$; EC, electrical conductivity (in μS/cm) at 25°C; HARD, hardness of all samples from hand pump.
**Correlation is significant at 0.01 level; *Correlation is significant at 0.05 level.

found between (K, Ca and hardness) and Cl, Mg and Na, and with hardness and Mg in the case of pre-monsoon 2007. On the other hand, the positive correlation were observed in between (Cl, SO_4, Na, Ca, Ph and hardness) and HCO_3. Again, positive correlation were found between (Na and Ph) and Cl; the concentration of SO_4 maintained positive relationship with all other major variables except Na, K and pH in post-monsoon 2005, this might be the cause of occasional use of gypsum fertilizer for SO_4 in the groundwater. Positive relationship was found between Na and K for groundwater samples of post-monsoon in 2005, which supports the line of argument that groundwater samples are characterized by the dominance of alkalis and relative abundance of sulphate. The alkalis are almost always higher than the cumulative concentration of Ca + Mg. Values for Na and K are difficult to acquire through water-rock interaction alone, but the bulk of it is evidently due to anthropogenic influences. Whereas, potassium (K) is a component of NPK (nitrogen, phosphorous and potash) fertilizer used abundantly in the study area and Sodium (although not part of this fertilizer combination), may find its way as impurities in some of the fertilizers, particularly urea.

In the case of post-monsoon (2005) groundwater samples (Table 4), a strong correlation was found between HCO_3 and (Cl, SO_4, Na, Ca, pH, hardness). A similar result was also observed in HCO_3 with SO_4, Ca, Mg, EC, hardness in pre-monsoon 2007. These might be the cause of application of fertilizer, pesticides, agricultural activities and other industrial units during these periods. But in case of pre-monsoon in 2006, a positive correlation was observed in Na, Mg, and hardness only.

Once again, it can be concluded that for pre-monsoon in 2006, the negative correlation were experienced between Cl and all other major variables except for the variable Na. From Tables 4, 5 and 6, it is shown that, there exist positive relation between K and Na, but between Na and Cl, the correlation was found to be negative in the case of the pre-monsoon in 2007.

Generally, it was fact that Pearson correlation coefficients were found higher than partial correlation coefficient for groundwater samples for major variables except for Na in post-monsoon in 2005, pre-monsoon in 2006 and pre-monsoon in 2007. In general, it can be concluded that, the post-monsoon period seems to be characterized by relative dilution in comparison to pre- monsoon.

In order to discover the relationships between TDS and major cations and anions, water properties regression model was used in this study. The way the eight variables

Table 6. Partial and Pearson correlation coefficient for groundwater samples (pre-monsoon 2007).

	HCO_3	Cl	SO_4	Na	K	Ca	Mg	EC	pH	HARD
Partial correlation coefficient for groundwater samples										
HCO_3	1.000									
Cl	-0.323	1.000								
SO_4	0.129	-0.390	1.000							
Na	0.387	-0.107	0.0665	1.000						
K	0.109	-0.543	-0.150	0.096	1.000					
Ca	-0.002	-0.509	-0.225	0.042	0.028	1.000				
Mg	-0.419	0.364	-0.169	-0.848	-0.216	-0.339	1.000			
EC	0.024	-0.155	0.042	-0.299	-0.191	0.313	0.158	1.000		
pH	0.227	-0.248	0.185	0.029	0.075	0.062	-0.103	0.0370	1.000	
HARD	0.325	-0.520	0.177	0.638	0.240	0.507	-0.853	0.0544	0.170	1.000
Pearson correlation coefficient for groundwater samples										
HCO_3	1.000									
Cl	-0.159	1.000								
SO_4	0.195	-0.033	1.000							
Na	0.252	-0.338*	-0.155	1.000						
K	0.145	-0.310	-0.029	-0.021	1.000					
Ca	0.103	-0.025	0.091	-0.232	0.150	1.000				
Mg	-0.264	0.543**	0.096	-0.882**	-0.068	0.045	1.000			
EC	0.048	-0.046	0.101	-0.329*	-0.152	0.336*	0.206	1.000		
pH	0.214	-0.232	0.143	0.049	0.062	0.022	-0.113	0.029	1.000	
HARD	0.216	-0.623**	-0.042	0.706**	0.120	0.146	-0.879**	-0.010	0.175	1.000

pH, −log10H$^{+;}$ EC, electrical conductivity (in µS/cm) at 25°C; HARD, hardness of all samples from hand pump.
**Correlation is significant at 0.01 level; *Correlation is significant at 0.05 level.

were selected, such as, [Na], [K], [Ca], [Mg], [HCO_3], [Cl], [SO_4], were considered as independent variables and TDS as the dependent variable. R^2 were observed and an analysis of variance was estimated as well. In post-monsoon (2005), the regression analysis between TDS-Na, TDS-K, TDS-HCO_3, showed strong positive relationship (r = 0.802, 0.715 and 0.786 respectively), and moderate positive correlation with Cl ions (r = 0.579) and very low positive correlation (r = 0.055, 0.324 and 0.330) with Ca, Mg, and SO_4. In 2006 pre-monsoon, the regression analysis between TDS-Na and TDS-HCO_3, showed strong positive relationship (r = 0.909 and 0.776 respectively). There exist positive correlation with K ions (r= 0.623) and very low positive correlation (r= -0.422, 0.394, 0.451 and 0.445) with Ca, Mg, Cl and SO_4. The positive sign of the input coefficients and significant-values pertaining to these variables indicates that there is a positive relationship between TDS and elements of ground water properties ([Na], [K], [Ca], [Mg], [HCO_3], [Cl] and [SO_4]).

Regression analysis

The estimated equation for groundwater for post-monsoon 2005 is:

$$TDS = -0.646 + 1.1007\ Na + 1.009\ K + 1.013\ Ca + 1.025\ Mg + 0.998\ HCO_3 + 0.990\ Cl + 0.995\ SO_4 + \varepsilon_1 \quad (1)$$

The estimated equation for groundwater for pre-monsoon 2006 is:

$$TDS = 0.806 + 0.996\ Na + 1.006\ K + 0.970\ Ca + 1.001\ Mg + 1.001\ HCO_3 + 0.999\ Cl + 1.000\ SO_4 + \varepsilon_2 \quad (2)$$

Where, ε_1 and ε_2 are the errors of estimation in regression model.

All the coefficients of input variables that is all water properties are statistically significant. In case of post-monsoon in 2005 (Table 7), almost all the variables of Pearson correlation coefficients were recorded at 1 to 10% level of significance. The multiple R coefficients indicated that, the multiple coefficient of correlation among major anion properties and TDS was observed moderate (the multiple R > 0.99). According to R^2 statistic, 100% for the total variance for the estimation of TDS is explained by the linear regression model. The R^2 and adjusted R^2 were observed to be 100% fit in themodel while Durbin Watson showed 1.758. The lower band and upper band of 95% confidence interval was found positive, indicating that all the variables are fit to each other. Once more, in case the of pre monsoon in

Table 7. Estimated chemical parameters of a linear regression model (post-monsoon 2005 and pre-monsoon 2006).

Model	Coefficients (B)	Std. error	Sig.	95.0% confidence interval for B	
				Lower bound	Upper bound
Post-monsoon (2005)					
(Constant)	-0.646	0.703	0.366	-2.084	0.792
Na	1.007	0.005	0.000	0.996	1.017
K	1.009	0.025	0.000	0.957	1.060
Ca	1.013	0.010	0.000	0.991	1.034
Mg	1.025	0.012	0.000	1.002	1.049
HCO_3	0.998	0.002	0.000	0.994	1.001
Cl	0.990	0.006	0.000	0.977	1.003
SO_4	0.995	0.002	0.000	0.990	0.999
R^2	1.000				
Adjusted R^2	1.000				
Durbin-Watson	1.758				
Pre-monsoon (2006)					
(Constant)	0.806	0.624	0.207	-0.471	2.082
Na	0.996	0.006	0.000	0.983	1.009
K	1.006	0.010	0.000	0.986	1.025
Ca	0.970	0.017	0.000	0.934	1.005
Mg	1.001	0.015	0.000	0.971	1.031
HCO_3	1.001	0.003	0.000	0.995	1.007
Cl	0.999	0.006	0.000	0.987	1.010
SO_4	1.000	0.002	0.000	0.996	1.004
R^2	1.000				
Adjusted R^2	1.000				
Durbin- Watson	2.158				

a Dependent variable: TDS.

2006 (Table 7), Pearson correlation coefficients values of all chemical properties were observed at 1 to 10% level of significance. The R^2 and adjusted R^2 are 100% fit in the model while Durbin Watson showed 2.158. The lower band and upper band of 95% confidence interval was positive which indicated all the variables are fit to each other.

Conclusion

Seasonal variation in the concentration levels of chemical and physical parameters of groundwater was successfully studied using a descriptive statistical measure and a partial correlation analysis. Almost all the chemical variables showed significant difference in the mean concentration level, except pH and Cl in case of groundwater samples. Mean values of chemical properties including anion and cation are not affected by extreme values in pre-monsoon and post-monsoon seasons. Na and HCO_3 were observed more consistent having less variation with standard deviation values (0.09613) and (0.07185) for the pre-monsoon periods of 2006 and 2007 respectively. On the other hand, Cl and Ca both showed more variation from the mean concentration among the chemical properties. From the partial correlation coefficient analysis of groundwater samples, dominance of alkalis and relative abundance of SO_4 during the post-monsoon was inferred. In the case of groundwater samples, the positive correlation between Na and K; among HCO_3 with Cl, SO_4, Na, Ca, pH, hardness were observed in the post-monsoon (2005) samples, and similar results were also observed among HCO_3 with SO_4, Ca, Mg, EC, hardness in pre-monsoon (2007) samples. But in case of pre-monsoon (2006) samples, positive correlation was found between HCO_3 and Na, Mg, hardness only. Generally, the post-monsoon period seemed to be characterized by relative dilution in comparison to pre-monsoon period. This study showed that statistical analysis is a useful method that could assist decision makers in measuring seasonal variations of groundwater samples.

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