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Research Article

Statistical Modeling of Groundwater Quality for Source and Ionic Relationships: A Case Study for Drinking Water Quality

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Abstract: A study was conducted to check the ground water quality of the University of Engineering and Technology (UET) campus, Lahore during October 13, 2014 to November 10, 2014. For this purpose grab samples were collected from four tube wells and eight end users for five weeks. These samples were analyzed for chloride (Cl^-), total dissolve solids (TDS), fluoride (F^-), pH, electrical conductivity (EC) and heavy metals (Cr, Pb, Ni, Fe) using prescribed methods and Atomic Absorption Spectrophotometer, respectively. Statistical tools were used for the source and correlation of ground water quality. Symmetrical (Cl^-, pH, EC, F^-, TDS, Ni, Fe) and non-symmetrical (Cr, Pb) distribution was observed. The Spearman and Pearson correlation matrix showed a correlation among heavy metals and physical parameters. Analysis of Variance (ANOVA) results also supported this correlation. The Principal Component Analysis (PCA) and the Cluster Analysis (CA) data identified four sources of chemical species in ground water, i.e. landfill leachates, emissions from vehicles, seepage of industrial emissions and tanneries wastewater, which enhanced the levels of heavy metals contamination in groundwater. Enrichment factor (EF) also indicated anthropogenic activities for the elevated levels of heavy metals in the ground water. The mean concentration of Cr (0.52 mg L^{-1}), Pb (0.08 mg L^{-1}) and Ni (0.08 mg L^{-1}) were higher than the permissible values while that of Fe was within permissible limit for drinking purposes.

Keywords: Heavy metals, physical parameters, Statistical Analysis, ground water, drinking water quality, ionic relationships, spatial and temporal contaminant variation

1. INTRODUCTION

The contamination of ground water is a critical issue throughout the world and several studies have been conducted to assess the severity of the problem [1-5]. Ground Water could be polluted by physical (pH, temperature, turbidity etc.) or chemical parameters (heavy metals, Fl, etc.) [3, 5-7]. The presence of heavy metals has been attributed to groundwater aquifer or through anthropogenic activities [1, 5, 8, 9]. The heavy metals in water pose serious issues due to their toxic and carcinogenic characteristics not only for drinking but for other life sustaining activities [9].

Earlier studies on groundwater of Lahore have exposed some critical facts that exacerbates the situation revealing serious levels of contaminants [1, 2, 10], like high levels of TDS and EC. Similarly, the industrial areas are more prone to contamination of groundwater [5] with high levels of Cd, Cr, Fe, As, Pb and Zn [2]. In order to have a clear idea of quality of groundwater, statistical modeling of groundwater was done for various physical and chemical parameters. The data were used for modeling to identify the source of emission and extent of anthropogenic activities. For this purpose various statistical tools like the Descriptive Statistics, the Box and Whisker plots, the Pearson and Spearman Correlations, Analysis of Variance (ANOVA), Principal Component Analysis (PCA) and Cluster Analysis (CA) were performed using SPSS IBM software. Enrichment

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Factor (EF) was calculated to ascertain the effects of anthropogenic activities for heavy metals.

2. MATERIALS AND METHODS

2.1 Study Area

Lahore is the second largest city of Pakistan with a population of 7.566 Millions in 2011 [11]. The water supply for domestic, industrial and commercial uses mainly comes from the groundwater which is estimated at 3.79, 0.92 and 0.77 MCM/day, respectively. The ground water quality of Lahore has been deteriorated due to excessive water use, untreated wastewater discharge into rivers and open dumping of un-segregated solid waste [12, 13]. To check the quality of ground water in terms of pollution levels, for source identification and correlation, an educational institute the University of Engineering and Technology (UET) Lahore was selected. Distribution system and sewerage system of UET is still the same from time of establishment, i.e. the year 1921. There is a tannery only 2-3 km away, a waste water and solid waste disposal point ≈ 1-2 km away from the UET campus which could be assumed major sources of ground water pollution (Fig. 1). Sampling sites (four tube wells) were selected in whole university. These were taken as source and eight different locations (Tap water supplied from these tube wells) were considered as end users (Table 1).

Table 1. Description of water sampling locations.

Location	Location Symbol	No. of Samples
Annaxie tube well (direct, 690 ft depth)	TW-1	5
Annaxie juice center (tap)	L-2	5
Annaxie (before entering)	L-3	5
Tube well behind shopping center (direct, 625 ft depth)	TW-4	5
Sultan Mehmood Ghaznavi hostel (tap)	L-5	5
Inside shopping center (tap)	L-6	5
Staff colony tube well (direct, 653 ft depth)	TW-7	5
40-B Staff colony, Operator's house	L-8	5
R-94 Staff colony (tap)	L-9	5
Tube well Khadija hall (direct, 715 ft depth)	TW-10	5
Khadija Hall hostel (tap)	L-11	5
GSSC UET (tap)	L-12	5

2.2 Sampling

Grab samples were taken from tube wells which were pumped sufficiently (10 min) in order to ensure that they represented the ground water. Samples from distribution system were taken after

Fig. 1. Google map showing locations of water samples.

flushing the lines sufficiently (30 min) ensure that samples were representative of supply system [6, 14]. Sampling was done from October 13, 2014 to November 10, 2014 in which a total of 60 samples were collected; 5 samples from each location with an interval of one week. This interval of one week was selected to have a good idea of quality of water. There can be changes in aquifer due to some weather conditions and geological conditions proving longer time the best for the sake of analytical study. Samples were collected with care to avoid any contamination that might cause any uncertainty in results.

2.3 Analytical Procedures

After sampling, the collected samples were analyzed in the laboratory for different parameters using standard methods [15].

3. RESULTS AND DISCUSSION

Different statistical tools like Descriptive Analysis, Box & Whisker Diagrams, Spearman's and Pearson's Correlation Coefficient, ANOVA, PCA and CA were applied to check the time based variation on water quality and finding the ultimate sources of contamination.

3.1 Descriptive Analysis

The Descriptive Statistics in the forms of mean, variance (V), standard deviation (SD), standard error (SE), median, range of variation, and percentile at 95 %, 75 % and 25 % (P95 %, P75 %, P25 %) has been computed [1] which is shown in Table 2. The mean value of Cl (186.89 mg L^{-1}), pH (7.55), Fl (0.332 mg L^{-1}) and TDS (519.46 mg L^{-1}) were within the permissible values of WHO (Table 2). The mean values of Cr, Pb, Ni and Fe were 0.518, 0.083, 0.079 and 0.091 mg L^{-1}, respectively. The values of Cr, Pb, and Ni exceeded the permissible limits by WHO while that of Fe was within limits set for taste detection (Table 2) [6]. The smaller values of standard error and standard deviation for the measured parameters reflected that the samples were more representative of the overall study area. The values of skewness (close to zero but not exactly zero) reflect symmetrical and non-symmetrical distribution of parameters among locations.

3.2 Distribution Patterns

In the Box Whisker plots data remain symmetrical if the data are evenly split at the median, and data will be asymmetrical or skewed if median is either right or left side of plots [7]. The results of Box Whisker graphs (Fig. 2) show that data is not normally distributed and there is a lot of un-symmetry in data. Median ranges for each parameter are different in every week. The Cl, pH and F showed negative skewness. The EC showed

Table 2. Descriptive statistical data for all the parameters for the sampling period (n=60).

Parameter	Cl (mg L^{-1})	pH	EC (µS cm^{-1})	F (mg L^{-1})	TDS (mg L^{-1})	Cr (mg L^{-1})	Pb (mg L^{-1})	Ni (mg L^{-1})	Fe (mg L^{-1})
Mean	186.89	7.55	791.08	0.33	519.47	**0.52**	**0.08**	**0.08**	0.09
Standard Error	11.86	0.04	35.88	0.01	32.03	0.13	0.03	0.01	0.01
Median	166.77	7.46	756	0.3	469	0.01	0	0.09	0.03
Standard Deviation	91.86	0.34	277.92	0.07	248.09	1.01	0.21	0.06	0.11
Skewness	0.16	0.68	0.32	0.54	0.42	1.54	2.7	-0.15	0.86
Minimum	40.02	6.96	339	0.2	142	0	0	0	0
Maximum	366.88	8.52	1396	0.5	1020	2.66	0.96	0.17	0.34
WHO Guidelines [6]	250	6.5-8.5	---	1.5	1000	0.05	0.01	0.02	---

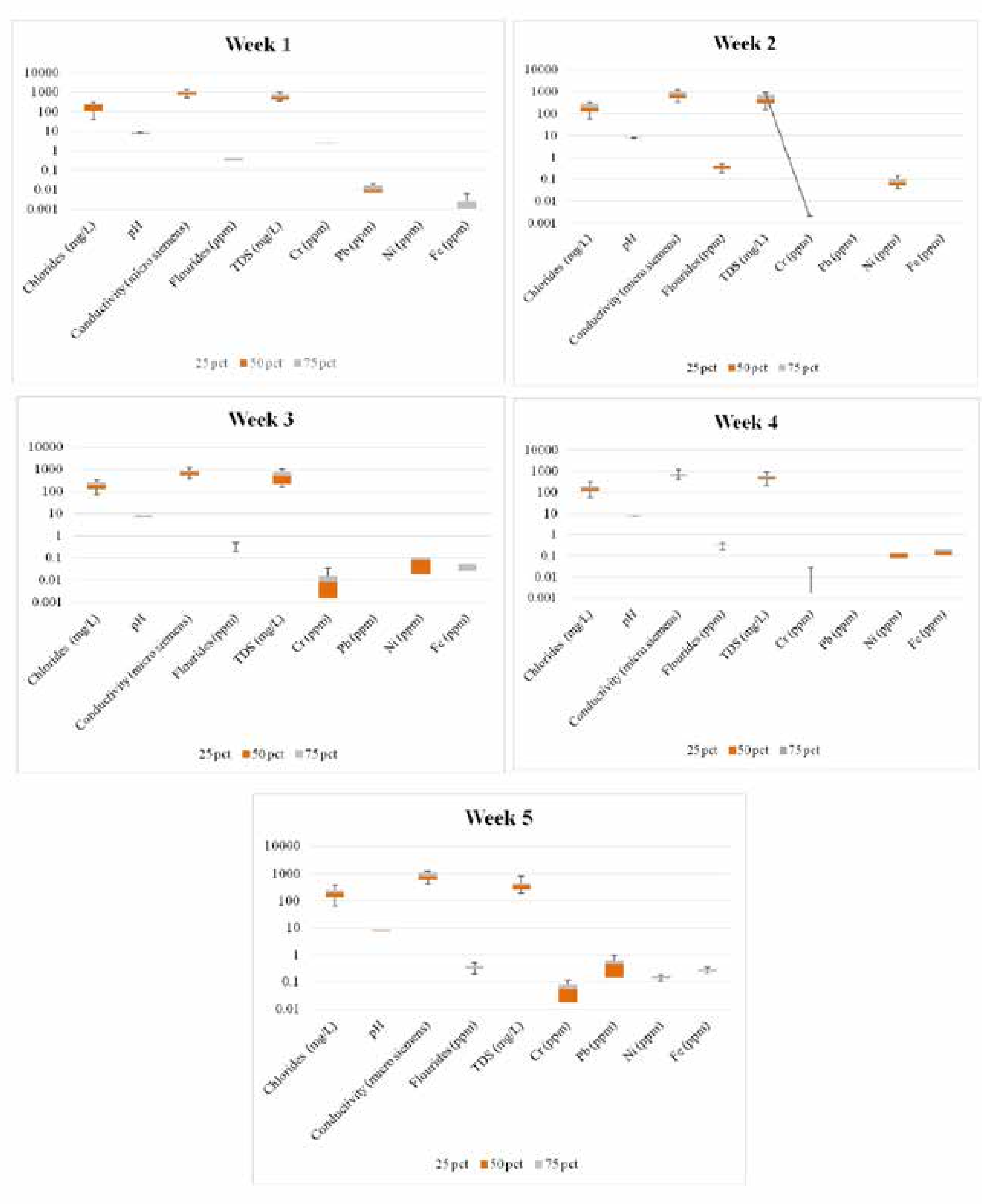

Fig. 2. Box and Whisker plots for five weeks of water sampling.

Table 3. Spearman correlation coefficient matrix (r-values) among all the parameters for five weeks of sampling.

	Cl^-	pH	EC	F	TDS	Cr	Pb	Ni	Fe
				Week-1					
Cl^-	1								
pH	-0.639*	1							
EC	0.884**	-0.554	1						
F^-	-0.231	0.54	-0.358	1					
TDS	0.663*	-0.428	0.804**	-0.307	1				
Cr	-0.701*	0.476	-0.501	-0.128	-0.116	1			
Pb	-0.637*	0.432	-0.466	-0.103	-0.018	0.958**	1		
Ni	0	0	0	0	0	0	0	1	
Fe	-0.07	-0.251	0.029	0.214	-0.149	-0.124	-0.12	0	1
				Week-2					
Cl^-	1								
pH	-0.743**	1							
EC	0.921**	-0.594*	1						
F^-	-0.853**	0.651*	-0.846**	1					
TDS	0.942**	-0.622*	0.965**	-0.796**	1				
Cr	0.131	0.131	0.044	0.19	0.218	1			
Pb	0	0	0	0	0	0	1		
Ni	-0.088	-0.049	0.06	-0.019	0.144	-0.044	0	1	
Fe	0	0	0	0	0	0	0	0	1
				Week-3					
Cl^-	1								
pH	-0.825**	1							
EC	0.930**	-0.822**	1						
F^-	-0.831**	0.752**	-0.840**	1					
TDS	0.837**	-0.746**	0.844**	-0.755**	1				
Cr	-0.538	0.676*	-0.646*	0.472	-0.678*	1			
Pb	0.039	-0.067	0.09	0.201	0.147	0.011	1		
Ni	0	0	0	0	0	0	0	1	
Fe	-0.569	0.194	-0.476	0.289	-0.356	0.39	0.096	0	1
				Week-4					
Cl^-	1								
pH	-0.771**	1							
EC	0.752**	-0.760**	1						
F^-	-0.279	0.185	-0.277	1					
TDS	0.661*	-0.238	0.531	-0.416	1				
Cr	0.378	-0.175	0.514	-0.199	0.239	1			
Pb	0	0	0	0	0	0	1		
Ni	-0.204	0.023	0.046	-0.301	0.14	-0.57	0	1	
Fe	-0.837**	0.613*	-0.664*	0.517	-0.552	-0.395	0	0.042	1
				Week-5					
Cl	1								
pH	-0.659*	1							
EC	0.648*	-0.309	1						
F	-0.732**	0.588*	-0.388	1					
TDS	0.746**	-0.372	0.51	-0.583*	1				
Cr	-0.757**	0.214	-0.545	0.54	-0.727**	1			
Pb	-0.702*	0.214	-0.515	0.596*	-0.658*	0.963**	1		
Ni	-0.074	0.207	-0.378	0.184	0.007	0.238	0.273	1	
Fe	0.081	-0.509	0.133	-0.219	0.091	0.378	0.441	-0.147	1

* Significant at 0.05 level (2-tailed).
** Significant at 0.01 level (2-tailed).

Table 4. Pearson correlation coefficient matrix (r-values) for all the parameters for five weeks of sampling (n=60).

	Cl^-	pH	EC	F	TDS	Cr	Pb	Ni	Fe
				Week 1					
Cl	1								
pH	-0.805**	1							
EC	0.957**	-0.779**	1						
F	-0.226	0.359	-0.322	1					
TDS	0.664*	-0.567	0.811**	-0.384	1				
Cr	-0.757**	0.634*	-0.572	-0.176	-0.103	1			
Pb	-0.699*	0.574	-0.548	-0.059	-0.016	0.912**	1		
Ni	0	0	0	0	0	0	0	1	
Fe	0.198	-0.231	0.181	0.054	-0.044	-0.17	-0.237	0	1
				Week 2					
Cl	1								
pH	-0.765**	1							
EC	0.959**	-0.795**	1						
F	-0.760**	0.855**	-0.831**	1					
TDS	0.949**	-0.688*	0.930**	-0.701*	1				
Cr	-0.608*	0.739**	-0.618*	0.492	-0.620*	1			
Pb	0	0	0	0	0	0	1		
Ni	0.211	0.009	0.157	0.02	0.317	0.169	0	1	
Fe	-0.408	0.096	-0.288	0.042	-0.325	0.352	0	0.033	1
				Week 3					
Cl	1								
pH	-0.702*	1							
EC	0.958**	-0.638*	1						
F	-0.834**	0.732**	-0.822**	1					
TDS	0.957**	-0.623*	0.984**	-0.822**	1				
Cr	0.195	0.148	0.042	0.165	0.148	1			
Pb	0	0	0	0	0	0	1		
Ni	-0.171	-0.07	-0.071	-0.049	-0.017	-0.1	0	1	
Fe	0	0	0	0	0	0	0	0	1
				Week 4					
Cl	1								
pH	-0.742**	1							
EC	0.922**	-0.604*	1						
F	-0.532	0.192	-0.521	1					
TDS	0.757**	-0.326	0.767**	-0.447	1				
Cr	0.348	-0.146	0.333	-0.137	0.155	1			
Pb	0	0	0	0	0	0	1		
Ni	-0.066	0.23	0.086	-0.332	0.162	-0.589*	0	1	
Fe	-0.864**	0.736**	-0.744**	0.532	-0.48	-0.368	0	0.028	1
				Week 5					
Cl	1								
pH	-0.708*	1							
EC	0.673*	-0.404	1						
F	-0.741**	0.545	-0.303	1					
TDS	0.795**	-0.475	0.607*	-0.623*	1				
Cr	-0.741**	0.368	-0.615*	0.502	-0.712**	1			
Pb	-0.682*	0.309	-0.52	0.512	-0.607*	0.966**	1		
Ni	0.039	0.083	-0.35	-0.038	0.103	0.107	0.107	1	
Fe	0.253	-0.453	0.163	-0.336	0.36	0.232	0.368	0.09	1

* Significant at P= 0.05 level (2-tailed).
** Significant at P= 0.01 level (2-tailed).

positive skewness in week-4 and negative during remaining weeks. The TDS reflected negative skewness in week-2 and 5 and positive during the remaining weeks. The Cr and Pb showed positive skewness in almost all weeks. The Ni and Fe gave positive skewness in first 3 weeks and negative skewness in weeks-4 and 5. Overall, there is little symmetry in data (Fig. 2).

3.3 Pearson Correlation Coefficients

The results of Spearman's correlation coefficients were performed by SPSS using two-tailed correlation and revealed that the Cl have strong negative correlation with pH, F and Pb while strong positive correlation with EC, TDS and Cr. Similarly, pH showed moderate negative correlation with EC. It also showed strong positive correlation with First two weeks and moderate positive in last two week. This variation indicated some anthropogenic activities affecting the ground water quality [12]. The pH showed moderate negative correlation with TDS while moderate positive correlation with Cr and Pb. The EC showed moderate negative correlation with F while, it showed strong positive correlation with TDS. The EC showed moderate negative correlation with Cr and moderate negative correlation with Pb. Fluoride showed moderate negative correlation with TDS while it showed moderate positive correlation with Cr. Similarly, TDS showed moderate negative correlation with Cr in one week and strong negative correlation in one week. TDS also showed moderate negative correlation with Fe while Cr showed strong positive correlation with Pb. The variations among correlation indicate that these physicochemical parameters, affecting the quality of ground water, are not originating from the same source; otherwise it showed strong correlations which are supportive of the effect of anthropogenic activities [4, 7, 12].

3.4 Spearman Correlation Coefficients

Chloride showed strong negative correlation with pH, strong positive correlation with EC while Chloride showed strong negative with F. It showed strong positive correlation with TDS while strong negative correlation with Cr. Chloride indicated moderate negative correlation with Pb in one week while strong negative in other week. Chloride indicated moderate negative correlation with Fe in one week and strong negative correlation in one week. Similarly, pH showed moderate negative correlation with EC and it showed moderate positive correlation with F. pH showed moderate negative correlation with TDS, moderate positive correlation with Cr, moderate positive correlation with Fe in one week but moderate negative correlation in the other week. The EC showed moderate negative correlation with F in two weeks and strong negative correlation in the other two weeks. The EC indicated strong positive correlation with TDS while moderate negative correlation with Cr, moderate negative correlation with Pb and Ni. Fluoride showed moderate negative correlation with TDS but moderate positive correlation with Cr. The TDS showed moderate negative correlation with Cr in one week and strong negative correlation in the other one week and moderate negative correlation with Fe. Similarly, Cr exhibited strong positive correlation with Pb and moderate positive correlation with Fe.

3.5 Analysis of Variance (ANOVA)

The ANOVA was used to evaluate the relationships between metals and other parameters. For this two null hypothesis (H_o) was formulated, i.e. heavy metals don't have any correlation with physiochemical parameters, i.e., Cl, EC, F, pH or TDS at $\alpha < 0.05$ and there is no correlation among physicochemical parameters. The results of ANOVA, physicochemical parameters are shown in (Table 5). It revealed that Cl has some correlation with pH and F. Pearson and Spearman correlation also supported these findings. The ANOVA for heavy metals and physicochemical parameters (Table 6) revealed that metals have correlation with EC and TDS due to their high ionic solubility, but have no correlation with other parameters.

Table 5. Analysis of variance for correlation of chlorides with physical parameters.

ANOVA		
Physical Parameters	Chloride Effect	
	F value	Significance
pH	1.203	1.581
F	0.325	0.125

Table 6. Analysis of variance for correlation of physical parameters with heavy metals.

Metal	Cl		EC		F		pH		TDS	
	F	Sign.*	F	Sign.*	F	Sign.*	F	Sign.*	F	Sign.*
Cr	5.043	0	0.459	0.899	0.854	0.471	0.661	0.858	0.309	0.923
Pb	2.195	0.025	0.542	0.851	1.865	0.146	0.944	0.438	0.325	0.916
Ni	2.859	0.005	0.442	0.909	0.438	0.727	0.786	0.74	0.273	0.939
Fe	1.523	0.145	1.041	0.582	0.218	0.884	0.538	1.102	0.947	0.256

*Significant at $P = 0.05$

3.6 Principal Component Analysis (PCA)

The PCA is based on an imaginary Eigen values. In the present study, all the Eigen values < 1 were ignored. The components having Eigen value > 1 are grouped based on same source. The PCA using rotation method of Varimax and Kaiser Normalization was performed and the results have been shown below in Table 7. The tool was applied on all the parameters for source identification. The PCA gave three components named as PC 1, PC 2 and PC 3 which explained a total of 78.329 % of variance. The PC 1 explained the highest share (39.43 %) of the total variance followed by PC 2 (27.01 %) and PC 3 (11.87 %). The PC 1 expressed the highest loading for Cl, EC, F and TDS which reflected seepage to groundwater aquifer from sewage effluent discharges, urban runoff, industrial waste discharges and contamination form refuse leachate to the ultimate problem. Moreover, dissolution of salt deposits in the aquifer can increase chloride levels and waters in the areas of Palaezoic and Mesozoic sedimentary rocks have higher TDS levels, ranging from as little as 195 to 1100 mg L^{-1} [16]. The PC 2 showed the highest loading for Pb and Fe which indicated dissolution of rocks and minerals in the aquifer or anthropogenic activities like seepage of wastewater from pigments, ammunition, caulking, cable sheathing, iron related industries, acid mine drainage and landfill leachates as sources. The PC 3 showed maximum loading for Cr which reflected contamination from the seepage of industrial emissions and tanneries wastewater [6].

Table 7. Principal Component loadings for water quality parameters using Varimax with Kaiser Normalization.

Rotated Component Matrix[a]			
Parameter	Component		
	1	2	3
Cl	0.909	-0.019	0.047
pH	-0.599	0.026	0.307
EC	0.866	0.101	0.371
F	-0.781	0.165	0.19
TDS	0.865	-0.168	0.213
Cr	0.051	-0.103	0.899
Pb	-0.161	0.93	-0.001
Ni	0.011	0.534	-0.733
Fe	-0.008	0.81	-0.429

Table 8. Enrichment factor for heavy metals for five weeks taking crustal average of Fe as reference.

Metals	Week 1	Week 2	Week 3	Week 4	Week 5
Fe	1	1	1	1	1
Cr	115.5	137.6	164.0	97.6	184.2
Pb	333.0	326.0	332.5	442.3	333.9
Ni	351.6	347.7	393.6	361.9	308.5

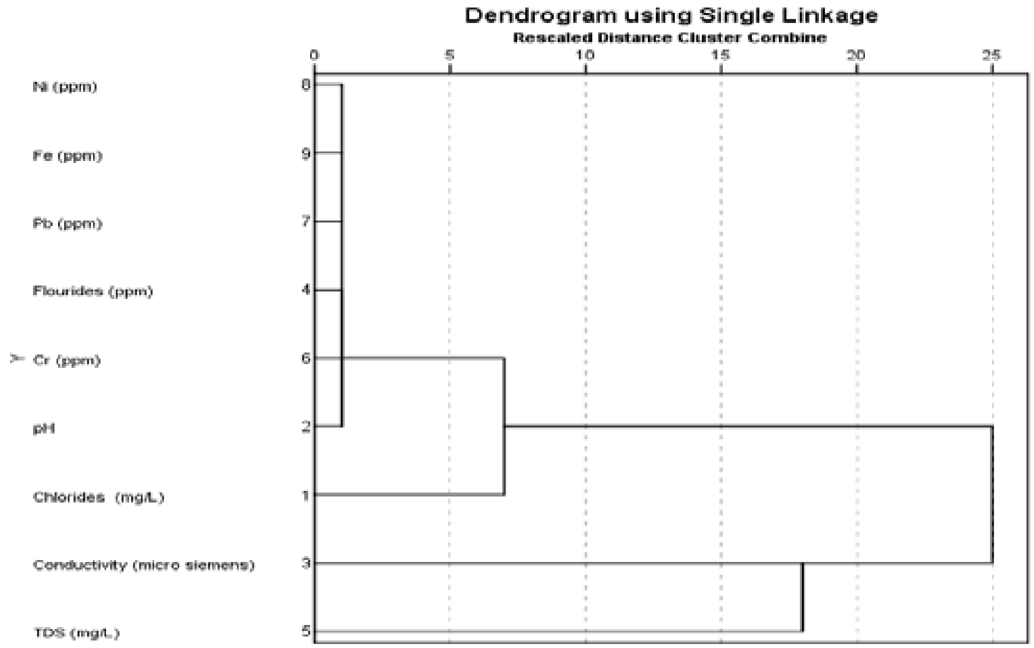

Fig. 3. Dendrogram of all parameters using Cluster Analysis showing various grouping on the basis of correlations.

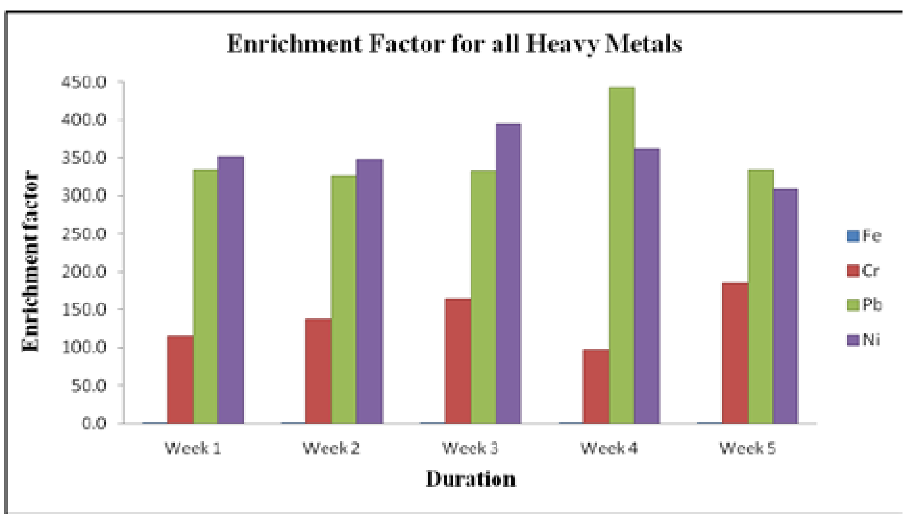

Fig. 4. Enrichment factor for all heavy metals using Fe as reference metal. It showed that the anthropogenic activities were responsible for contamination of groundwater.

3.7 Cluster Analysis (CA)

A tree diagram shows the agglomerative hierarchical clustering algorithms available in the data and is called Dendrogram [7]. The extent of correlation among parameters using Cluster analysis Dendrogram (single linkage) has been performed on average values of each parameter on all the 12 locations (Fig. 3). These groups were formed on the basis of CA, i.e., G_1, G_2 and G_3. The Ni, Fe, Pb, F, Cr and pH formed a single group (G_1). Euclidean distance was less so it showed strong relation as is evident in the Fig. 3 and in the results of PCA. The EC and TDS formed another group (G_2), Euclidean distance was more, so relation can be supposed as weak. Third group was formed by G_1 and Cl (G_3) relation was not too strong. The G_2 and G_3 groups are distinct from each other (Fig. 3) having large euclidean distance which reflect that both have different sources. The Dendrogram relationship indicated that investigated heavy metals have strong correlation among themselves and poor correlation with other physicochemical parameters.

3.8 Enrichment Factor for Trace Metals

To calculate the extent of anthropogenic activities for relative increase in trace metals concentration; Enrichment Factor (EF) was measured. Enrichment factor of metals relative to earth crust composition was calculated. It demonstrated that the metals concentration increased due to human activities. The EF was computed by knowing the mean concentration of metals in earth crust and in samples of study area [15]. The Fe levels were taken as reference for enrichment factor calculation in this study and EF were calculated by using following relationship:

$$EF = \frac{\left(\frac{C_{Me}}{C_{Fe}}\right)Sample}{\left(\frac{C_{Me}}{C_{Fe}}\right)Crust} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots (1)$$

where C_{Me} represents the concentration of metal, which is to be compared with concentration of Fe.

Trace metals having EF values ≤ 5 are not considered as enriched because some degree of uncertainty is present in the composition of the Earth crust [17]. Elements having EF values 10-100 are moderately enriched and have sources other than the Earth crust while metals having EF values ≥ 100 are highly enriched and have different sources of emission, i.e. anthropogenic activities [17]. The EF values of Fe, Cr, Pb and Ni are shown in Table 8. All the values are > 100 during the study period (five weeks) strongly supporting anthropogenic activities to be the sources of heavy metals (Fe, Cr, Pb, and Ni) in the groundwater. The order of EF is in the increasing order of Pb > Ni > Cr > Fe.

4. CONCLUSIONS

The analysis of groundwater quality has been done for important parameters and statistical analysis was performed for source identification and correlation. The following conclusions could be drawn on the basis of study:

- The concentration of physical parameters and Fe among heavy metals was found within WHO guidelines but the concentration of Cr, Pb, and Ni remained higher than their respective permissible limits.
- The concentration of metals was in the decreasing order of Cr > Pb > Ni. Concentrations of Cl, pH, EC, F, TDS, Ni and Fe showed almost symmetrical distribution while a little non-symmetrical trend was recorded for Cr and Pb.
- Spearman and Pearson correlation showed that Ni, Cr, Pb and Fe have low correlation with physical parameters. The ANOVA results reflected that physical parameters were associated with heavy metals except Cl which effected metals; and showed relation only with Fe amongst all the heavy metals present.
- The PCA and CA data identified various anthropogenic and natural sources for the enhanced levels of heavy metals in water samples from UET campus. The assumed sources identified included vehicular emissions, acid mine drainage, landfill leachates, seepage of industrial emissions and tanneries wastewater in the aquifer as the sources of contamination (Fig.1).
- Enrichment Factor showed moderate and higher contribution to heavy metals by anthropogenic activities and trend observed was Pb > Ni > Cr > Fe.
- Environmental rules and legislations should be strictly implemented and industries should be forced to dispose wastewater after treatment in compliance with the available standards of the country. Community should be given awareness on importance of wastewater treatment and safe disposal of the resulting effluent. Septic tank can be best option in such localities the effluent of which can be disposed into some nearby drain.

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