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CHEMISTRY

Multivariate statistical analysis of heavy metals and physico-chemical parameters in the groundwater of Karak District, Khyber Pakhtunkhwa, Pakistan

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Abstract. Groundwater heavy metal pollution is a major concern all around the world. For the assessment of heavy metals and physico-chemical characteristics, groundwater samples were collected from different locations of the Karak District, Pakistan. With the help of the global information system device (GIS), groundwater samples were collected and studied from 47 locations. The present study focused on the water table (WT), water source depth (WSD), pH, electrical conductivity (EC), dissolved oxygen (DO), total dissolved solids (TDS), lead (Pb(II)), silver (Ag(I)), iron (Fe(II)) and chromium (Cr(VI)) parameters. Heavy metals were analyzed by the Atomic Absorption Spectrophotometer (AAS). The Pearson's matrix of correlation showed relationships between several parameters, such as the EC and the TDS which had close interactions between all the three different groundwater samples (collected by hand pump (HP), bore holes (BH) and tube wells (TW)). The strong correlation was detected in all the sources of water between the TDS and the EC, the regression coefficient (*r*) of which was 1. In the hierarchical clustering (by dendrograms) the HP samples show two clusters: Cluster 1 contains seven parameters and Cluster 2 has four parameters. The BH samples have two clusters: Cluster 1 contains three parameters and Cluster 2 has eight parameters. The TW dendrogram also shows two clusters: Cluster 1 contains six parameters while Cluster 2 has five parameters.

Key words: groundwater, clusters analysis, heavy metals, correlations.

1. INTRODUCTION

Groundwater is the most diverse and significant global water reservoir, which contributes approximately 34 percent of the overall yearly water supply [1] that promotes public health, monetary incentives and natural diversity; and the accessibility is restricted in many cases. Although groundwater exists within complicated subsurface structures, it is not immediately visible on the surface of the Earth. It is also a variable source, which is complicated to quantify in both space and time. Thus, statistical evaluation, effective management and usage of groundwater are also

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important [2,3]. Typically, an interpretation of the effects of water quality has been performed on a single criterion, which prevents performing correlation on complexities and restricts simplicity estimations. On the other hand, the usage of a multivariate analysis jointly applying water quality parameters generates a detailed representation of the groundwater quality of a region based on certain interrelationships or correlations [4].

Contamination of groundwater involves point pollutants, residues and pollutants' discharges through factories, including furnaces and extraction, as well as non-point factors, including dissolved compounds (natural and artificial), the use of fertilizers and pesticides detected in the discharge of agricultural and urban sewage water and many more pollution sources [5]. Toxic and harmful heavy metals are used in the production of goods in several industries, such as textile and color/dye industries, paper production, food production industries, distilleries, refineries, chemicals factories, seafood production systems, pesticide industries and in the cement production. Pollutants are particularly present in small production plants in Bangladesh, where the pollutants are discharged completely untreated or partially treated into the river [5].

Multivariate statistical methods are effective tools to reduce the raw data about pollutants' migration and for the analysis of multi-components in physical and chemical assessments [6]. Multivariate statistical approach, including cluster analysis (CA) and factor analysis (FA), is a frequently utilized tool for analyzing water quality by drawing logical inferences [7–11]. Multivariate analysis is frequently used to classify and assess groundwater and it is valuable for the detection of regional differences induced by natural and anthropogenic sources [7,11,12].

The purpose of this analysis was to examine six physico-chemical parameters and important heavy metals in the groundwater samples from the Karak District, Pakistan. The broad data set collected was subjected to multivariate CA and FA techniques to evaluate information on similarities and dissimilarities between the various sampling sites; to classify water quality variables for spatial dissimilarity; and to determine the effect of the contamination factors on the water quality parameters.

2. MATERIAL AND METHODS

2.1. Study area

In the Karak District, Pakistan, the arid and semi-arid regions were the study zone of the research. Karak lies in the southern part of Khyber Pakhtunkhwa. The geological location of the study sites was 33°7′12″N, 71°5′41″E. The area is rocky with deep valleys and interconnected spurs. Karak is an arid region with an estimated yearly rainfall of around 320–330 millimeters, which can change periodically and have different intensities [13]. The present research was planned to determine the correlations between physical and chemical parameters and selected heavy metals in the groundwater of the Karak District.

2.2. Sampling

The groundwater samples were collected in the field by three different methods (hand pump, bore holes and tube wells) using the Global Positioning System (GPS) within the study area. Overall, 47 groundwater samples were collected from the study zone. Among these 47 samples, 12 samples were collected by hand pump, 21 by bore holes and 14 samples were collected from tube wells. The overall collected groundwater samples were collected into clean, sterilized and air-tight 2-liter polyethylene bottles. Aqua regia (concentrated nitric acid and concentrated hydrochloric acid in a molar ratio of 1:3) was used for the dissolving and fixing of all metals in the samples.

2.3. Method of analysis

Physical tests of groundwater, such as pH (781 pH Meter, Metrohm AG, Herisau, Switzerland), electrical conductivity (EC Thermo Fisher, USA), total dissolved solids (TDS), temperature (Temp) and dissolved oxygen (DO) (with a DO Meter Thermo Fisher, USA) were performed in the field. Temperatures of the collected water samples were also checked with the help of thermometer. The selected heavy metals (HMs), including lead (Pb(II)), silver (Ag(I)), iron (Fe(II)) and chromium (Cr(VI)) were measured by the Atomic Absorption Spectrometer (Perkin Elmer, AAS-PEA-700, USA) under the measuring protocol of the Department of Chemistry, Abdul Wali Khan University Mardan, Khyber Pakhtunkhwa, Pakistan.

2.4. Statistical analysis

For mathematical and statistical analysis Microsoft Excel (ver. 2007) and IBM SPSS 26 were used in this study. During the collection of water samples, the GIS device (eTrex10, Garmin, Kansas City, USA) was employed and the study site maps were created on the ArcMap (ver. 10.5) (Fig. 1).

3. RESULTS AND DISCUSSION

3.1. Groundwater parameters

Different metals were analyzed in groundwater samples to assess the pollution level caused by heavy metals. The

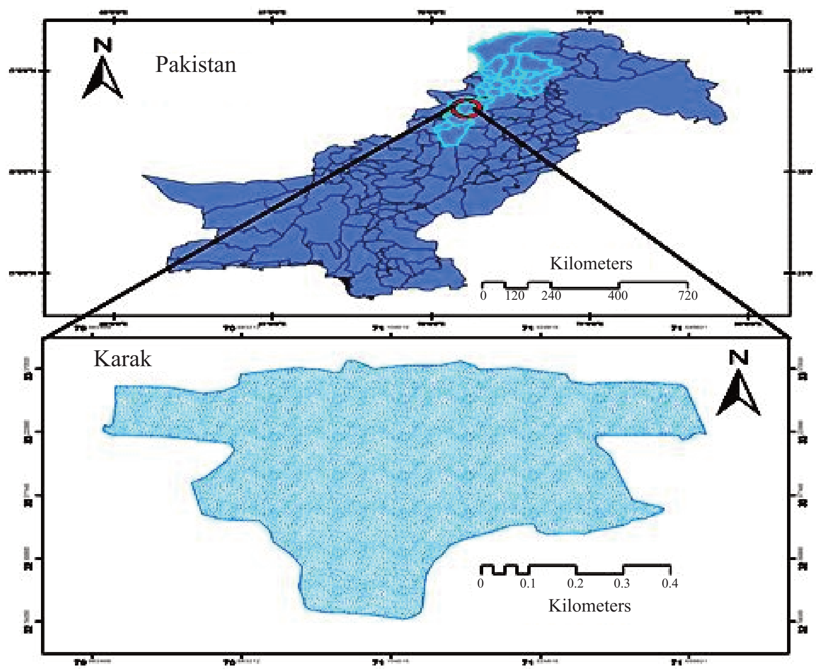

Fig. 1. Site of sampling in the Karak District, Pakistan.

analyzed metals included lead (Pb(II)), silver (Ag(I)), iron (Fe(II)) and chromium (Cr(VI)) as some of the most toxic metals affecting human health.

The permissible limit of Pb(II) in groundwater suggested by the WHO and the Pakistan Council of Research in Water Resources (PCRWR) is 0.01 mg/L [14,15]. The concentration of Pb(II) in the HP water samples ranged from 0.65 mg/L to 2.65 mg/L, in the BH water samples it was between 0.3 mg/L and 4.6 mg/L and in the TW water samples the concentration was in the range of 0.35 mg/L and 7 mg/L, as shown in Table 1.

The investigation showed that silver (Ag(I)) also constituted an important part in the collected water samples (Fig. 2). The permissible limit of Ag(I) in groundwater samples is 0.025 mg/L. This limit has been suggested by the PCRWR and the WHO [14,15]. The concentration of Ag(I) in the water samples of the HP was detected from 0.105 mg/L to 0.113 mg/L, in the BH groundwater samples it ranged from 0.103 mg/L to 0.114 mg/L, while in the TW groundwater samples it was between 0.103 mg/L and 0.192 mg/L, which exceeds the permissible limit for the research zone and may affect the local communities.

In general, Fe is a prevalent element in the Earth's crust, mainly in the form of ferro-magnesium silicates, as well as being a significant element in certain soils [16]. The limit of iron (Fe(II)) recommended by the WHO and the PCRWR in groundwater is 0.3 mg/L [15,17]. The concentration of iron (Fe(II)) in the groundwater samples collected by the HP from the research zone ranged from 0.98 mg/L to 7.07 mg/L, in the BH groundwater samples it was between 0.69 mg/L and 6.65 mg/L while the concentration of Fe(II) in the TW water samples was in the range of 0.51 mg/L and 5.22 mg/L, as shown in Table 1. The concentration of Fe(II) often exceeded the permissible limits suggested by the WHO and the PCRWR.

Chromium (Cr) occurs in a trivalent form, which seems to be a balanced and non-hazardous type, and in another shape, i.e. hexavalent chromium – chromium that poses a threat to health. Trivalent chromium types are seldom present in drinking water [15]. The limit of Cr(VI) in groundwater suggested by the PCRWR and the WHO is 0.05 mg/L [14,15]. In the study area the concentration of Cr(VI) in the HP water samples was detected in the range of 0.05 mg/L and 0.16 mg/L, Cr(VI) in the BH water samples ranged from 0.04 mg/L to 0.13 mg/L, while the concentration of Cr(VI) in the TW water samples was detected in the range of 0.03 mg/L and 0.2 mg/L, as shown in Tables 1–4.

3.2. Physico-chemical parameters in samples

It was reported that the depth and water table of individual water sources were mainly different. For the sampling by hand pump (HP) the water table (WT) was 7.6–43 m while the overall water source depth (WSD) was detected between 24–76 m. The bore hole (BH) sampling had a WT of 3.4–168 m and the WSD was 91–198 m. The tube well (TW) WT was 18–168 m while the WSD ranged from 37 to 213 m as shown in Table 1. The pH values showed the influence of the groundwater to respond to the alkaline

Table 1. Water table (WT), water source depth (WSD), physico-chemical parameters (pH, electrical conductivity (EC)), dissolved oxygen (DO) saturation, total dissolved solids (TDS) and heavy metals in different sources of the groundwater. Standard deviation (Std Dev) and relative standard deviation (RSD) are also indicated

	Groundwater samples' physico-chemical parameters											
	Variable	WT (m)	WSD (m)	pH	EC (μS/cm)	DO sat. (%)	Temp (°C)	TDS (mg/L)	Pb(II) (mg/L)	Ag(I) (mg/L)	Fe(II) (mg/L)	Cr(VI) (mg/L)
Hand pump	Min	7.6	24	7.53	559.3	51.3	29.6	374.7	0.65	0.105	0.98	0.05
	Max	43	76	8.31	7674	96.1	29.9	5141.6	2.65	0.113	7.07	0.16
	Median	15.4	46	7.97	1808.5	82.95	29.85	1211.7	2.1	0.11	2.1	0.095
	Mean	18	42	7.9	2103.3	78.6	29.8	1409.2	1.7	0.1	2.5	0.09
	Std Dev								0.8	0.002	1.6	0.029
	RSD								45.7	2.11	65	32.2
Bore hole	Min	3.4	91	7.34	449.4	54.1	29.5	301.1	0.3	0.103	0.69	0.04
	Max	168	198	8.64	6324	109.9	29.9	4237.1	4.6	0.114	6.65	0.13
	Median	37	76	7.73	1046	92.3	29.8	700.8	1.15	0.106	1.71	0.08
	Mean	51	83	7.82	2329.7	90.3	29.8	1560.9	1.5	0.11	2.11	0.08
	Std Dev								0.99	0.003	1.27	0.03
	RSD								67.9	2.53	60.3	31.2
Tube well	Min	18	37	7.6	351	91	29	235.2	0.35	0.103	0.51	0.03
	Max	168	213	8.44	9784	113.5	29.9	6555.3	7	0.192	5.22	0.2
	Median	116	175	8	871.5	100	29.8	584.0	1.85	0.109	1.485	0.105
	Mean	106	156	7.91	1370.9	100.1	29.7	918.5	1.88	0.12	1.69	0.1
	Std Dev								1.66	0.02	1.14	0.05
	RSD								88.3	20.98	67.1	47.2

content contained in the water. The collected groundwater samples had a different range of pHs maintained by different sources. The pH of the HP water samples was in the range of 7.53 and 8.31, the BH water samples had the pH between 7.34 and 8.64 while the pH of the TW water samples ranged from 7.6 to 8.44 (Table 1, Fig. 3). The permissible limit of the pH in fresh water specified by the WHO is between 6.5 and 8.5 [14]. The electrical conductivity (EC) of the collected water samples ranged from 559.3 μS/cm to 7674 μS/cm for the HP, the EC of the BH was detected from 449.4 μS/cm to 6324 μS/cm while in the TW water samples the EC was in the range of 351 μS/cm and 9784 μS/cm (Table 1). The range of the TDS in the HP water samples reached from 374.7 mg/L to 5141.6 mg/L. In the BH water samples the TDS ranged from 301.1 mg/L to 4237.1 mg/L while in the TW water samples the TDS was detected to be between 235.2 mg/L and 6555.3 mg/L (Table 1). Although high concentrations of the TDS can cause gastrointestinal effects in humans, they may also contribute to laxative effects. High TDS values can be linked to differences in geological compositions as well as to hydrological factors [18].

The dissolved oxygen (DO) parameter was also investigated in the water samples collected from the study area. In the HP water samples, the DO saturation values were detected in the range of 51.3% and 96.1%, in the BH water samples they were between 54.1% and 109.9%, while in the TW water samples the DO values were in the range of 91% and 113.5% [19]. Although the lack of DO in groundwater can be due to odoriferous anaerobic decomposition products [5], the concentration of DO (under 100% saturation) may also be affected by temperature as shown by Rajendran et. al. [20]. The temperature of the HP water samples was in the range of 29.6 °C and 29.9 °C, the temperature of the BH water samples was measured from 29.5 °C to 29.9 °C, while the TW water samples' temperature was detected in the range of 29 °C and 29.9 °C.

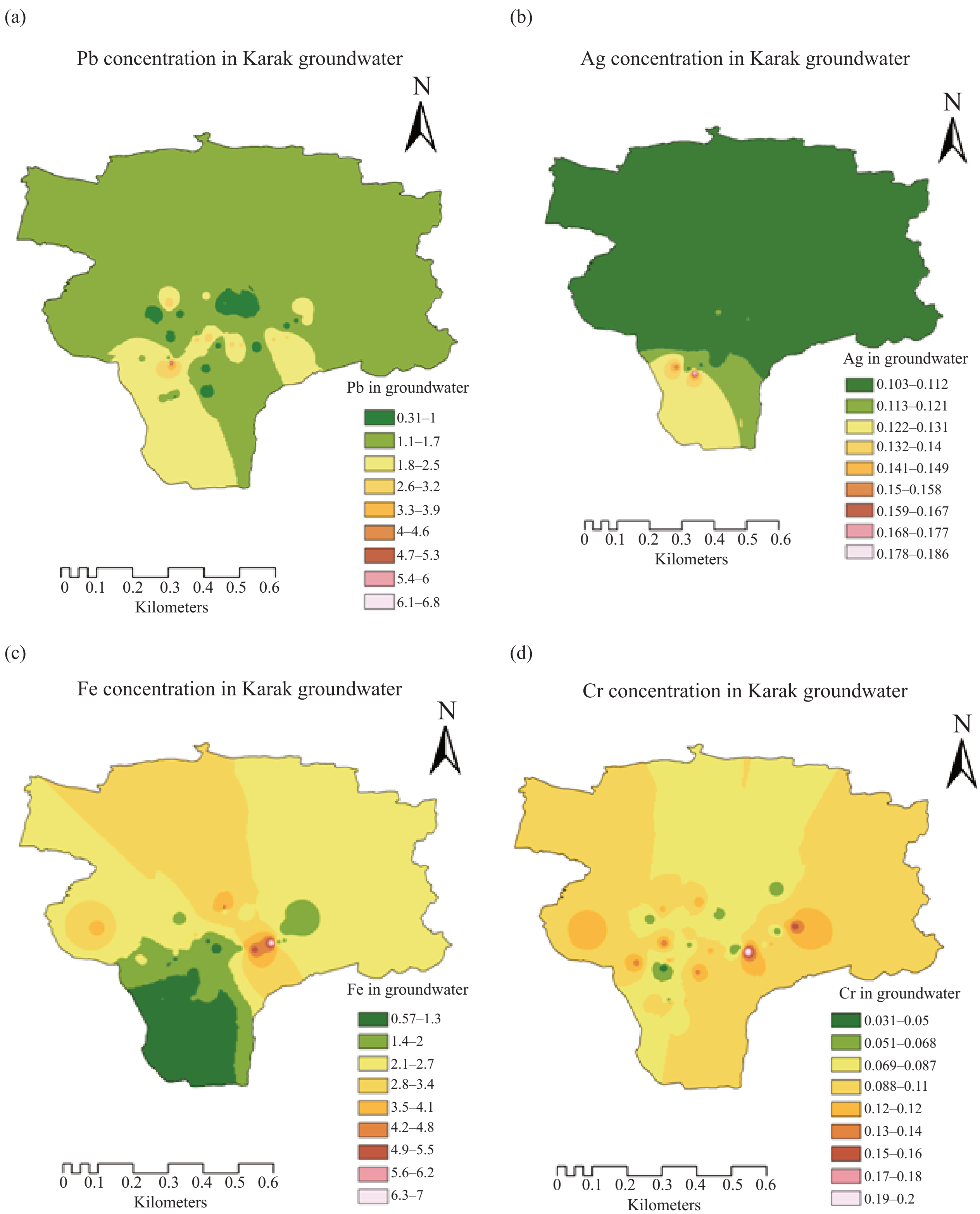

Fig. 2. Concentration of heavy metals (HMs) in mg/L in different groundwater samples: (a) – Pb(II), (b) – Ag(I), (c) – Fe(II), (d) – Cr(VI) concentration.

3.3. Correlation coefficient (r) analysis

The Pearson correlation analysis (PCA) findings for the physico-chemical parameters and the HMs in the groundwater of the research region were observed. The PCA results for the physico-chemical parameters and the HM content of the study zone are summarized in Tables 2, 3 and 4. The inter-element relations present valuable details on the origins and routes of the HMs and the physico-chemical parameters. The intensity r, known as a linear correlation coefficient, shows the frequency and existence of the statistically significant correlations between the two parameters. The linear correlation coefficient is also referred to as the Pearson product-moment correlation coefficient. The formula for the calculation of "r" is as follows:

$$r=\frac{n\sum xy-\left(\sum x\right)\left(\sum y\right)}{\sqrt{n\left(\sum x^2\right)-\left(\sum x\right)^2}\ \sqrt{n\left(\sum y^2\right)-\left(\sum y\right)^2}},$$

where n is the number of pairs of data.

The correlation coefficient ranges from +1 to –1. A correlation of +1 means a completely good relationship between the two parameters. When the significance of one variable increases, the significance of another parameter will increase at a parallel point. A correlation of –1 means when one variable varies inversely with another – as the

Table 2. Correlation matrix of HP water parameters in the study area, high correlations are shown in yellow

	WT	WSD	pH	EC	DO	Temp	TDS	Pb	Ag	Fe	Cr
WT	1										
WSD	0.625	1									
pH	0.096	–0.243	1								
EC	0.067	–0.061	–0.266	1							
DO	–0.041	–0.367	–0.379	0.115	1						
Temp	–0.632	–0.446	–0.189	–0.349	0.493	1					
TDS	0.067	–0.061	–0.266	1	0.115	–0.349	1				
Pb	0.465	0.470	–0.460	–0.221	0.222	–0.187	–0.221	1			
Ag	0.355	0.210	–0.109	0.241	–0.027	–0.631	0.241	0.549	1		
Fe	0.042	–0.189	–0.067	–0.007	0.515	0.269	–0.007	0.129	0.105	1	
Cr	0.573	0.864	–0.128	0.278	–0.372	–0.548	0.278	0.144	0.146	–0.207	1

Table 3. Correlation matrix of BH water parameters in the study area, high correlations are shown in yellow

	WT	WSD	pH	EC	DO	Temp	TDS	Pb	Ag	Fe	Cr
WT	1										
WSD	0.859	1									
pH	0.212	0.149	1								
EC	–0.240	–0.413	–0.193	1							
DO	0.371	0.379	0.461	0.066	1						
Temp	0.103	0.133	0.024	0.059	0.102	1					
TDS	–0.240	–0.413	–0.193	1	0.066	0.059	1				
Pb	–0.070	–0.104	–0.393	–0.215	–0.071	0.109	–0.215	1			
Ag	0.046	0.050	–0.010	–0.491	0.024	–0.113	–0.491	0.379	1		
Fe	–0.252	–0.054	–0.142	0.373	–0.038	0.047	0.373	–0.311	–0.501	1	
Cr	0.179	0.243	–0.180	0.167	0.070	–0.233	0.167	–0.235	0.050	–0.128	1

Table 4. Correlation matrix of TW water parameters in the study area, high correlations are shown in yellow

	WT	WSD	pH	EC	DO	Temp	TDS	Pb	Ag	Fe	Cr
WT	1										
WSD	0.815	1									
pH	0.314	–0.041	1								
EC	–0.169	–0.384	0.571	1							
DO	0.631	0.437	0.048	–2E-05	1						
Temp	0.159	0.324	0.415	1E-01	–0.168	1					
TDS	–0.169	–0.384	0.571	1	–1.1E-05	0.120	1				
Pb	0.170	0.212	–0.324	–0.209	0.449	–0.093	–0.209	1			
Ag	0.442	0.340	0.262	–0.125	0.042	0.056	–0.125	–0.013	1		
Fe	–0.736	–0.755	0.018	0.253	–0.349	0.087	0.253	–0.155	–0.254	1	
Cr	–0.390	–0.414	0.321	0.283	–0.325	0.550	0.283	–0.304	–0.156	0.720	1

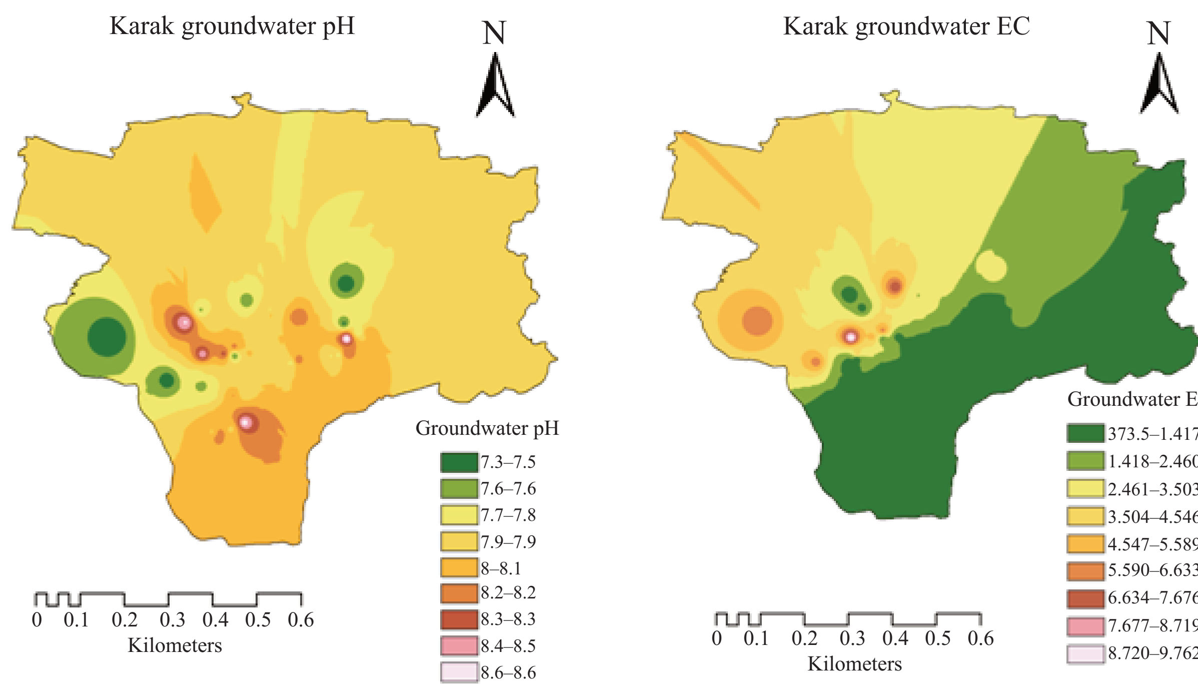

Fig. 3. The pH content and electrical conductivity (EC) of groundwater in µS/cm in different locations.

importance of one variable increases – the significance of all other variables will decrease at the same time. In fact, there is a continuum of worse than ideal interactions here between two values, like zero, which often implies that there is no interface between the two variables [21]. The terms powerful, center and commonly assigned towards "r" (correlation coefficient) value refer to a range >1, 1–0.864, 0.864–0.859, 0.859–0.815, 0.815–0.720, 0.720–0.631, 0.631–0.615.

The correlation between the HP water sample parameters is shown in Table 2. The correlation between the WT and the WSD is 0.625 (r), between the WSD and Cr it is 0.864 (r) while a strong correlation lies between the TDS and the EC, which is 1 (r). Table 3 shows the correlation between the parameters of the BH water samples. In Table 3, the relation between the WT and the WSD is 0.859 (r) while a strong correlation lies between the TDS and the EC, which is 1 (r). Table 4 displays the correlation between the parameters of the TW water samples. As demonstrated in Table 4, the relation between the WT and the WSD is 0.815 (r), for DO and the WT it is 0.631 (r), for Cr(VI) and Fe(II) it is 0.720 (r). The strongest relation is shown between the TDS and the EC, the value of which is 1 (r).

3.4. Hierarchical cluster analysis (HCA)

The Hierarchical Cluster Analysis (HCA) is a mixture of methods for classifying broad information into clusters at the level of similarity or dissimilarity. As a consequence, the resultant classes are identical to one another, yet different in certain categories. Investigators have also commonly used the HCA to identify water quality [22,23]. In the present study the HCA was applied to group samples and their similarities in water quality as well as to determine linkages across the water quality variables. The results of the HCA are given as dendrograms (Figs 4, 5 and 6). Figure 4 shows the dendrogram of the parameters of those water samples which were collected by the HP, Fig. 5 illustrates the BH dendrogram and Fig. 6 presents the dendrogram of the water samples which were collected from the TW in the research zone.

Among the HP water sample dendrograms there are two clusters. Cluster 1 contains seven parameters while Cluster 2 contains four parameters, as shown in Fig. 4. The BH dendrogram has two clusters. Cluster 1 contains three parameters while Cluster 2 has eight parameters, as shown in Fig. 5. Likewise, the TW dendrogram has two clusters. Cluster 1 contains six parameters while Cluster 2 has five parameters, as illustrated in Fig. 6.

The dendrograms using Ward Linkage are given in Figs 4, 5 and 6.

Different factors can be interconnected and have an effect on the groundwater and surface water quality. Studies have shown that landfill impacts the hydrological cycle and could cause groundwater pollution [24]. Likewise, phosphorus (P) has been considered a pollutant causing eutrophication in different water bodies when released into the environment untreated [25]. Earlier studies have also shown the effect of dissolved organic carbon (DOC), that it is dependent on the hydrological factors taking part in many biogeochemical reactions in Lake Võrtsjärv, Estonia [26].

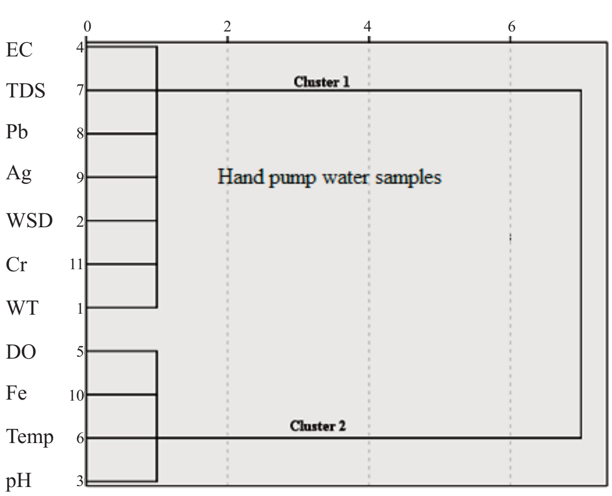

Fig. 4. HCA dendrogram (using Ward Linkage) of HP water parameters.

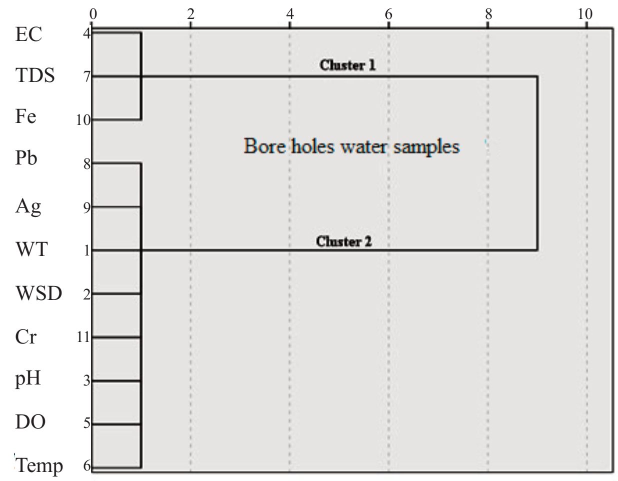

Fig. 5. HCA dendrogram (using Ward Linkage) of BH water parameters.

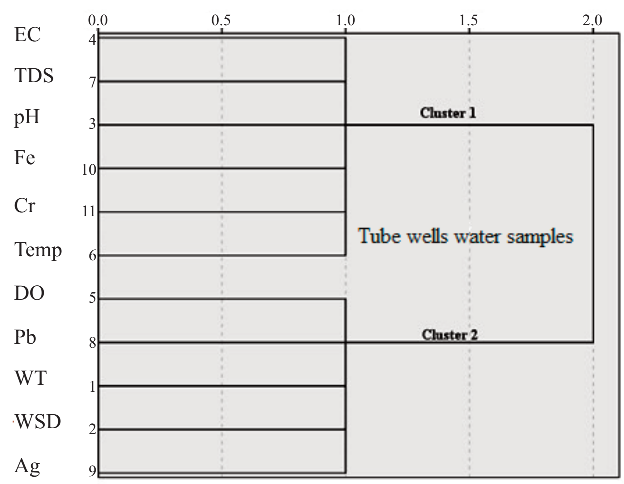

Fig. 6. HCA dendrogram of TW water parameters.

4. CONCLUSIONS

In this study different multivariate statistical tools were applied for the evaluation of three different groundwater sources (samples collected by HP, BH and TW) in the arid and semiarid regions of the Karak District, Khyber

Pakhtunkhwa, Pakistan. Different parameters (pH, EC, WT, WSD, TDS, DO, Pb(II), Fe(II), Cr(VI) and Ag(I)) were studied for the collected groundwater samples. Some parameters of those samples were beyond their permissible limits, suggested by the WHO and the Pakistan Council of Research in Water Resources. The permissible limits of Cr(VI), Ag(I) and Pb(II) in groundwater are 0.05, 0.025 and 0.01 mg/L, respectively, but often the limits were exceeded in the studied samples. The concentration of Cr(VI) in the HP water samples was detected in the range of 0.05 mg/L and 0.16 mg/L, Cr(VI) in the BH water samples was between 0.04 mg/L and 0.13 mg/L. The concentration of Ag(I) in the HP water samples ranged from 0.105 mg/L to 0.113 mg/L, in the BH groundwater samples it was from 0.103 mg/L to 0.114 mg/L, while in the TW groundwater samples it was detected from 0.103 mg/L to 0.192 mg/L. The concentration of Pb(II) in the HP water samples was between 0.65 mg/L and 2.65 mg/L, in the BH water samples it ranged from 0.3 mg/L to 4.6 mg/L and in the TW water samples the concentration range was detected between 0.35 mg/L and 7 mg/L. The minimum and maximum quantities of the physico-chemical parameters were in correlation between the matrices, showing strong relations between the parameters. Among all the parameters, the strongest relations were observed between the EC and the TDS.

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Pakistani Karaki piirkonna põhjavee raskmetallide ja füüsikalis-keemiliste omaduste mitme muutujaga statistiline analüüs

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Põhjavee raskmetallireostus on kogu maailmas suur probleem. Põhjaveeproovide analüüsimiseks võeti pinnase- ja veeproove raskmetallide ning füüsikalis-keemiliste omaduste hindamiseks Pakistanist Karaki piirkonna eri kohtadest. Globaalse infosüsteemi (GIS) abil koguti ja kaardistati 47 põhjavee ning pinnaseproovi asukohad. Uuringus keskenduti veetasemele (WT), veeallika sügavusele (WSD), pH-le, elektrijuhtivusele (EC), lahustunud hapnikule (DO), kogu suspendeeritud tahkele ainele (TDS), pliile (Pb), hõbedale (Ag), rauale (Fe) ja kroomi (Cr) parameetritele. Raskmetalle analüüsiti aatomabsorptsiooni spektrofotomeetriga (AAS). Pearsoni korrelatsioonimaatriks näitas seoseid mitme parameetri vahel, nagu elektrijuhtivus ja kogu suspendeeritud tahke aine, kuna need olid tihedas korrelatsioonis kõigi kolme erineva põhjaveekogumi vahel. TDSi ja EC vahel leiti tugev seos kõigist veeallikatest, mille regressioonikordaja (r) oli 1. Tehti ka hierarhilist klasterdamist (dendrogrammide järgi), kus proovid sisaldasid kuni 2 klastrit, milles oli kuni 8 parameetrit.