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## Evaluating groundwater nitrate and other physicochemical parameters of the arid and semi-arid district of DI Khan by multivariate statistical analysis

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### ABSTRACT

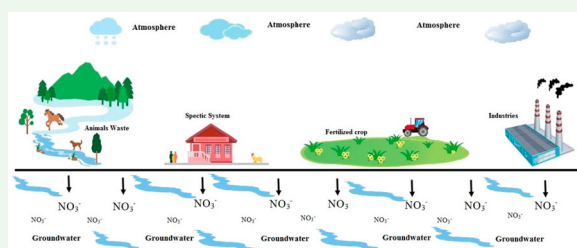
Nitrate as an important water pollutant, causing eutrophication was analyzed in Pakistan at different water sources (hand pump (HP), bore hole (BH) and tube well (TW)) to assess the contamination level caused by  $\text{NO}_3^-$ .  $\text{NO}_3^-$  concentrations in the HP water samples were  $31 \text{ mg L}^{-1}$  to  $59 \text{ mg L}^{-1}$ , in BH  $20 \text{ mg L}^{-1}$  to  $79 \text{ mg L}^{-1}$  while in TW water samples it was between  $29$  to  $55 \text{ mg L}^{-1}$ . The association of  $\text{NO}_3^-$  with other selected parameter in groundwater can be determined by using statistical approaches. Different physicochemical parameters (pH, electrical conductivity (EC), temperature and dissolved oxygen (DO)) were studied in groundwater samples of the research district. The Pearson correlation coefficient ( $r$ ) for groundwater characteristics were calculated. Hierarchical Cluster Analysis (HCA) was used to categorize samples based on their groundwater quality similarities and to find links between groundwater quality factors. The key relationship of the groundwater for HP samples on EC and TDS ( $r = 1$ ) had a great correlation, while all other parameters correlations were lower ( $r = 0.40$ ), BH's parameters on WT and WSD ( $r = 0.57$ ), WT and pH ( $r = 0.57$ ), EC and DO ( $r = 0.50$ ), DO and TDS ( $0.50$ ), EC and TDS ( $r = 1$ ) had a quite high correlation, while all other parameters correlations were less than ( $r = 0.40$ ), on the other hand, tube well parameters on TDS and EC ( $r = 1$ ) had a perfect correlation, DO and pH ( $r = 0.75$ ) parameters correlations were less than ( $r = 0.40$ ).

### ARTICLE HISTORY

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### KEYWORDS

Groundwater; nitrate; Hierarchical Cluster Analysis; ion chromatography



## Introduction

Groundwater is often regarded among the finest and also the most essential sources of drinking water [1, 2]. In many arid and semi-arid regions of the world, where surface water is of low quality and scarce, groundwater is widely used for daily consumption and in agriculture [3]. Furthermore, it is estimated that more than 1.5 billion people around the world rely on groundwater for basic requirements such as drinking and irrigation [4–6]. Groundwater reserves have significantly declined in its quality and quantity in several arid and semi-arid

regions around the world since the mid-twentieth century. Less groundwater reserves are present due to the industrial and agricultural development, expanding urbanization, population growth, inadequate sanitation, pollutant runoff, lack of adequate water quality monitoring, seasonable precipitation patterns and anthropogenic activities [6, 7]. However, in recent years, groundwater contamination in arid and semi-arid regions of the world has increased dramatically [5, 8].

Hydrocarbons, synthetic organic compounds, mineral cautions, mineral anions, viruses, and radionuclides are

among the materials that have been reported as pollutants in groundwater. Nitrate and nitrite are ions that occur naturally as part of the nitrogen cycle [9]. Nitrate is a chemical component that can damage health, potable water, and can create undesirable health consequences on consumers when it is in soluble form [10, 11]. Water pollution caused by industrial and municipal waste, animal manure and fertilizer, or industrial and municipal wastewater can all lead to nitrate contamination of water resources [12, 13]. Because of pollution of water with organic elements, breakdown of urban and industrial waste in the soil, washing of animal and chemical manures generated by agricultural activities, and sewage leakage, polluted water may reach groundwater resources when it migrates through layers of the earth [14, 15]. What is certain is that nitrate in water can cause carcinogenesis, congenital birth problems, cardiovascular disease, high blood pressure, and impacts on the nervous system [16, 17]. As a result, WHO [18] has issued guidelines in this area. As a result, Pakistan has sought to establish the maximum permitted content (standard) of nitrate and nitrite in drinking water at 45 and 3 mg/L, respectively [19]. Multivariate statistical techniques can be a useful means to interpret and represent information about the groundwater constituents and geochemistry [20].

To present a quantifiable assessment of similarity of water quality indices and to propose the fundamental natural and anthropogenic activities in groundwater reservoirs, multivariate statistical methods, such as principal component analysis (PCA) and hierarchical cluster analysis (HCA) have been applied. Multivariate statistical analysis is a collection of statistical approaches or algorithms that can be used in a variety of sectors of empirical research. These technologies are also improving our understanding of the groundwater system's physical and chemical properties in location and time [21–23].

The relation of nitrates with other selected parameter in water can be determined by using statistical approaches. Dendrogram models are one of the most prominent statistical methods for predicting groundwater. It's a multivariate analytical model that can explain the link across groundwater quality and other variables [24].

### A risk to the environment and human health

Human healthcare risks assessments are critical tasks that aid in determining the possible negative impact of pollutants on public health after prolonged interaction with specific chemical agents [25–27]. Nitrates are mostly absorbed by the human through the drinking of water [5, 27]. World Health Organization (WHO) has specified a nitrate guideline concentration value of 45 mg/L,

beyond that, water is unsafe for use [28]. The increase of nitrate levels in groundwater can have many negative effects on public health, such as methemoglobinemia can be caused by a higher nitrate consumption [29].

Idiopathic causes by nitrates are more common in younger children (under 26 weeks). There has been determined decreased cytochrome b5 reductase quantities in red blood cells after exposure to nitrates [30]. Whenever these patients acquire significant metabolic acidification as a result of diarrhoea and exhaustion, methaemoglobinemia can occur [31]. An important hazardous element for causing newborn methemoglobinemia is the use of nitrate-contaminated drinking water. As a result, newborns have a strange blue-grey skin tone and, based on the intensity of childhood disease, it may become restless or lethargic. If the illness is not diagnosed and treated promptly, it can quickly progress to coma and mortality [32].

The purpose of research investigation was to use multivariate statistics to better identify the factors that could influence groundwater resources and to see if  $\text{NO}_3^-$  had an effect on HP, BH and TW water quality.

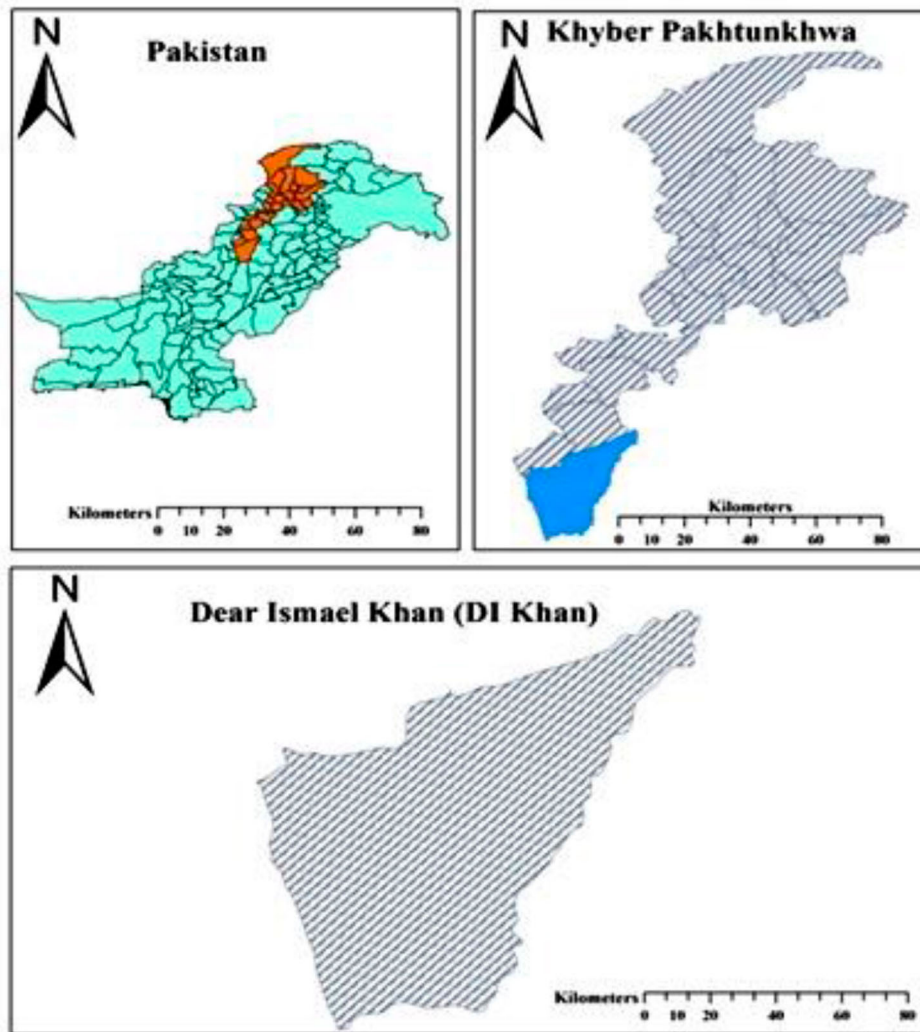
## Materials and methods

### Study area

The study area was an arid and semi area of district Dera Ismail Khan (DI Khan) Khyber Pakhtunkhwa Pakistan. The study sites geological location is 31°86'26" North, 70° 90'19" East. Most of the DI Khan district is rocky with deep valleys and interconnected spurs. DI Khan is an arid region with an estimated yearly rainfall of around 230–268 millimetres, which can change periodically and have different intensities [33]. The current research work has been planned to determine the correlation between nitrate, physicochemical parameters and other selected heavy metals in the research zone of Khyber Pakhtunkhwa (Figure 1).

### Data preparation

Nitrate, temperature, electrical conductivity (EC), pH, water table (WT), water source depth (WSD), total dissolved solids (TDS) and dissolved oxygen are among the key water quality characteristics investigated in the study. Each of the study's parameters has shown a probable association with nitrate distribution. The solution's acidity or alkalinity is measured by pH. A restricted pH range is required for chemical reactions inside aquatic organisms for survival and growth. DO denotes the amount of oxygen dissolved in water, which is required by aquatic life. Inadequate oxygen in water can cause



**Figure 1.** Study area.

issues like reduced microorganism growth. Some metals are necessary for life, while others are extremely harmful. Metal concentrations that are required by some organisms may be hazardous to others[34].

Temperature affects the chemistry and functioning of aquatic species, making it one of the most essential water quality parameters. Dissolved ions, which act as conductors are dependent on the salinity as a measure of the concentration of salts present in the water. Although soluble ions enhance influence both- salinity and conductivity, the two measurements are linked[35].

Nitrates are reduced to nitrite mostly by microbes and, to a lesser extent, by mammals' enzymes in organs. Several mechanisms exist in the blood and tissues to convert nitrite to NO and other physiologically significant nitrogen oxides. While getting engaged by glutamate synthase and integrated into carbon lattices as detailed previously for transport further in plants, nitrate is firstly reduced to nitrite and then to ammonia[36].

### **Sampling and parameters**

The ground water samples were collected in the field by three different methods (hand pump (HP), boreholes (BH) and tube wells (TW)) using a global position system (GPS) within the study area. Overall, 31 underground water samples were collected from the study zone. Within these 31, 11 samples were collected by a hand pump, 9 by boreholes and 11 samples were collected from tube wells. The overall collected ground-water samples were collected into clean, sterilized and air-tight 1-liter polyethylene bottles.

### **Physicochemical of analysis**

Physical tests of the groundwater samples, such as pH (781-pH metre, Metrohm AG, Herisau, Switzerland), electrical conductivity (EC ThermoFisher-US), total dissolved solids (TDS), temperature (Temp) and dissolved oxygen

(DO-metre ThermoFisher-US) were performed in the field. While, the nitrate analysis water sample was kept in an icebox under their measuring protocols and transported to the Department of Chemistry, Abdul Wali Khan University Mardan, Khyber Pakhtunkhwa, Pakistan.

### **Ion chromatography**

In aqueous solutions, ion chromatography was used for analyses of typical anions and cations. Ion-exchange resins use their interaction with the resin to separate atomic or molecule ions. Aqueous solutions must be used, and filtration or dilution may be required. In the case of solid material, ions are extracted using water. Most of the ion chromatography equipment have multiple mobile phase reservoirs with different pH buffers, as well as a programmed pump that can vary the mobile phase's pH throughout the separation.

### **Statistical analysis**

For mathematical and statistical analysis Microsoft Excel (ver. 2007), GMDH Shell and IBM SPSS 26 were used in this present study. During the collection of water samples GIS device Etrex 10, Garmin was used and maps were created on ArcMap (Ver. 10.5).

### **Hierarchical Cluster Analysis**

HCA was used to evaluate the regional variables in groundwater in terms of water quality metrics. In clustering analysis, the uses of single linkage as part of the strategies for discovering natural groupings in multi-variate data. A single linkage system divides a data set into clusters based on one or more parameters, making the data as similar as achievable inside every

cluster and as diverse as reasonable between clusters [37].

## **Results and discussion**

### **Nitrate in DI Khan groundwater samples**

Anions were analysed from groundwater samples to assess the pollution level caused by nitrate. Nitrate ( $\text{NO}_3^-$ ) was investigated in the three different sources of groundwater, such as hand pumps, boreholes, and tube wells of DI Khan Khyber Pakhtunkhwa.

Nitrate complex has several uses like as in fertilizer, as an oxidizing agent in explosives and in the glass, enamel, metallurgy and alloy industries. Nitrate complex that is also soluble in water releases nitrate ions that can develop a state that decreases the capability of blood to bring oxygen [38]. Nitrate compounds amounts are up to 163 million pounds released per each year. The acceptable limit of nitrate in the groundwater to be used for drinking is 50 mg/L [39, 40]. While, the concentration of nitrate in almost all natural water sources are less than 10 mg/L. In most cases, the level of nitrates more than 25 mg/L showing that man-made activities pollution of the water sources [41, 42].

The level of nitrate in the HP water sample was found to be from 31 mg/L to 59 mg/L, in BH it was from 20 mg/L to 79 mg/L while in TW water the nitrate level was detected in the range of 29 mg/L to 55 mg/L that is also shown in Table 1.

### **Physico-chemical parameters of the DI Khan groundwater samples**

Different physicochemical parameters (pH), electrical conductivity (EC), temperature ( $^{\circ}\text{C}$ ) and dissolved oxygen (DO) were studied in groundwater samples of

**Table 1.** Nitrates and other physicochemical parameters from HP, BH and Tube wells different water sources.

Sources	Variable	WT	WSD	pH	EC	DO	Tem	TDS	$\text{NO}_3^-$
Hand Pumps	Min	20	90	7.09	925.1	33.8	29.6	620	31
	Max	68	185	7.98	3975	90.3	29.9	2663	59
	Median	55	125	7.65	2075	47.8	29.8	1390	45
	Mean	49.27	135.45	7.61	1841.93	57.32	29.79	1234.09	44.2
	Std. deviation			0.30	831.94	20.60	0.12	557.24	7.6
Sources	Variable	WT	WSD	pH	EC	DO	Tem	TDS	$\text{NO}_3^-$
Bore Holes	Min	40	150	6.67	921.5	39.3	29.6	617	20
	Max	125	850	7.95	6405	85.4	29.9	4291	79
	Median	86	185	7.49	2009	60.8	29.7	1346	61
	Mean	83.56	257	7.36	2353.94	60.64	29.72	1577	57.8
	Std. deviation			0.46	1582.22	18.10	0.11	1060.09	15.2
Sources	Variables	WT	WSD	pH	EC	DO	Tem	TDS	$\text{NO}_3^-$
Tube wells	Min	80	200	6.67	875.6	32.6	29	587	29
	Max	155	1100	8.16	4067	90.7	29.9	2725	55
	Median	120	870	7.65	2002	82	29.8	1341	48
	Mean	120.91	812.73	7.65	2145.51	71.77	29.62	1437.45	43.8
	Std. deviation			0.41	906.71	19.04	0.32	607.36	9.1

the research district. The changes of these parameters within the various depths of the groundwater can also be seen from the data shown in Figure 2. The temperature of the groundwater research area was found to be similar. The temperature of all collected groundwater samples was measured on-site. It was observed that the temperature of all groundwater samples was almost similar (29–29.9°C). Various studies have shown that local temperature affects the nature of groundwater [43].

Likewise, the pH of all groundwater samples was investigated onsite. The pH of HP groundwater samples was between 7.09 and 7.98, BH groundwater samples were between 6.67 and 7.95 and TW groundwater samples was in between 6.67 and 8.16 as shown in Table 1. The pH value can much affect the quality of groundwater, which can be further transferred to humans and other organisms. From the data collected, it is clear that most of the pH of the samples were within the acceptable range.

Dissolved oxygen (DO) is the necessary parameter of the water quality and is usually ranges from less than 1.0 mg / L (13.03% saturation) to more than 20 mg / L (260% saturation). It is linked with numerous significant roles, particularly in marine life. High DO level stand for good quality water in rivers, streams and lakes[44]. DO concentration vary with the season, depth and temperature. Mostly in summer, it is usually reduced as the

decomposition rate of organic matter increases[45]. DO levels were investigated in all groundwater samples collected from the research area. In HP water samples, DO was found from 33.8–90.3 mg/L, in BH water samples it was 39.3–85.4 mg/L and 32.6–90.7 mg/L in TW water samples as shown in Table 1. The collected data shows that the DO level in all samples is within the acceptable range and provides comfortable sustainability to humans, animals and plants.

Groundwater samples from HP, BH, and TW in the research area were also tested for electrical conductivity (EC). It is the current channel in water that is affected by total dissolved solids (TDS). In the HP water sample TDS was found from 620 to 2663 S/cm, in the BH water samples it was 617–4291 S/cm and in the TW water samples it was found in the range of 587–2725 S/cm, often exceeding the border value 1110 S/cm, suggested by the WHO [46]. The collected samples from HP, BH and TW were analyzed for EC and the obtained data were ranged from 925.1  $\mu$ S/cm to 3975  $\mu$ S/cm in HP water samples, 921.5  $\mu$ S/cm to 6405  $\mu$ S/cm in BH while 875.6  $\mu$ S/cm to 4067  $\mu$ S/cm in TW samples as shown in Table 1. The collected evidence indicates that the groundwater has engulfed a range of minerals and salts from the soil. The high level of EC has become noticed in all resources, which is a serious threat for plants, fauna, and humans[47] Figure 3.

### Correlation coefficient (r) analysis

The proportional association between two aspects is known as correlation. Whenever the quantity of one variable rise or drops in tandem with the values of another this is known as a strong correlation. When one parameter leads the other to grow, the correlation is said to be positive; when one parameter causes the other to drop, the correlation is said to be negative. Whenever the variables are in the ranges of +0.8–1.0 and –0.8 to –1.0, the correlation is stronger; whenever the variables are in the ranges of +0.5–0.8 and –0.5 to –0.8, the correlation is moderate; and when the parameters are in the range of +0.0–0.5 and –0.0 to –0.5, the correlation is poor[48].

Tables 2–4 show the values of the Pearson correlation coefficient ( $r$ ) for groundwater characteristics, water source depth, and water table. Groundwater samples revealed the stronger association groups. Major relation of the groundwater at just the degree of the HP water table EC and TDS ( $r = 1$ ) have perfect correlation, in the correlation while all other parameters correlations are less than ( $r = 0.40$ ) as shown in Table 2, borehole parameters are WT and WSD ( $r = 0.57$ ), WT and pH ( $r = 0.57$ ), EC and DO ( $r = 0.50$ ), DO and TDS (0.50), EC and

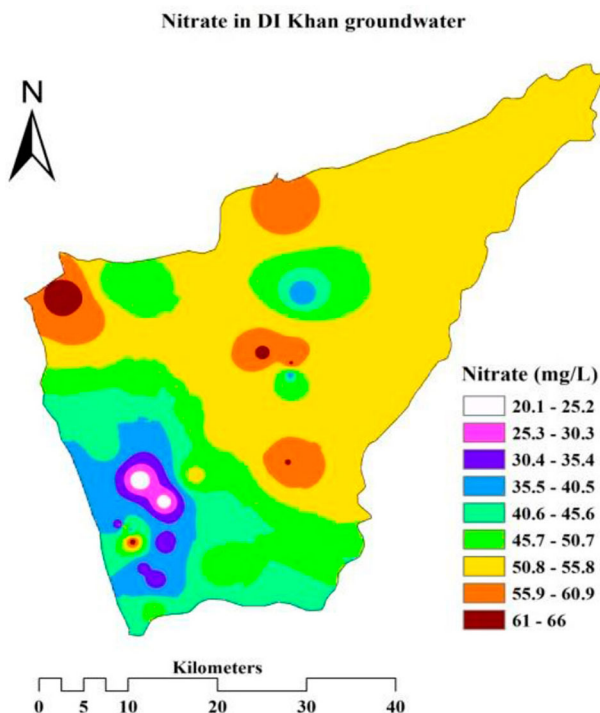
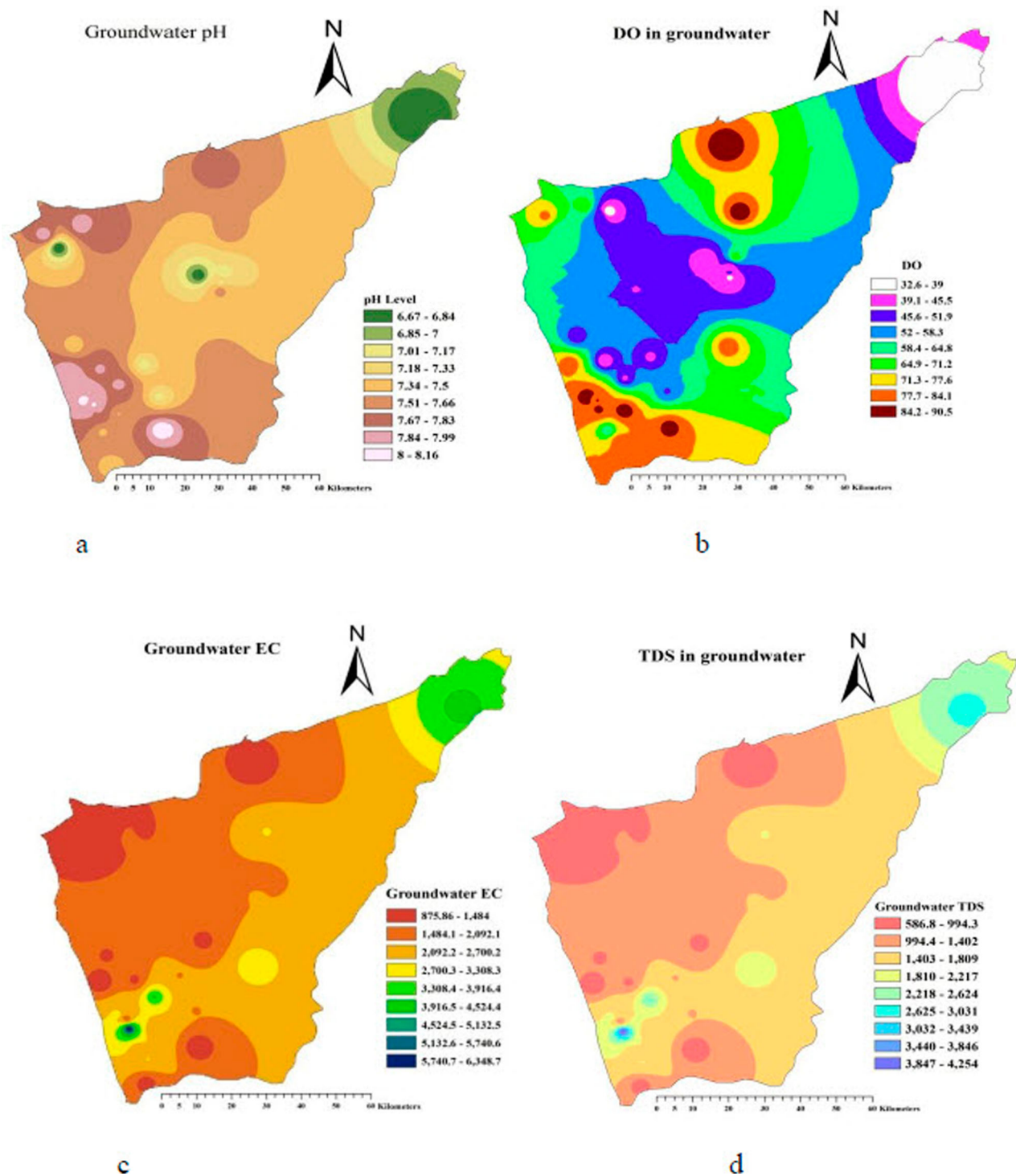


Figure 2. Concentrations of nitrates and its distribution in the groundwater at study area.



**Figure 3.** Concentrations and values of physico- chemical parameters a-pH, b-DO, c-EC, d-TDS.

TDS ( $r = 1$ ) have perfect correlation, while all other parameters correlations are less than ( $r = 0.40$ ) as shown in Table 3, on the other hand, tube well parameters are TDS and EC ( $r = 1$ ) have perfect correlation, DO and pH ( $r = 0.75$ ) while all other parameters correlations are less than ( $r = 0.40$ ) as shown in Table 4. Variable loading is represented as just a factor of correlation between both the variable and key factors. It might be

positive or negative indicating which is the contribution of different factors increases or reduces with rising loads in a sphere, respectively[49].

The Pearson correlation coefficient suggests a significant link between physicochemical and nitrate parameters. Whereas the findings of this study will support better managing polluted groundwater, in particular, to lessen the inherent risk to nearby residents.

**Table 2.** Correlation matrix of HP water samples in DI Khan.

		WT	WSD	pH	EC	DO	Tem	TDS	Nitrate
Hand Pumps	WT	1							
	WSD	0.46	1						
	pH	0.07	0.11	1					
	EC	0.29	-0.28	-0.18	1				
	DO	-0.04	0.28	0.26	-0.38	1			
	Tem	0.15	0.40	0.21	0.35	0.10	1		
	TDS	0.29	-0.28	-0.18	1	-0.38	0.35	1	
	Nitrate	0.24	0.11	-0.08	-0.20	-0.04	-0.16	-0.20	1

**Table 3.** Correlation matrix of BH water samples in DI Khan.

		WT	WSD	pH	EC	DO	Tem	TDS	Nitrate
Bore Holes	WT	1							
	WSD	0.57	1						
	pH	0.57	0.20	1					
	EC	0.40	0.22	0.30	1				
	DO	0.44	0.46	0.43	0.50	1			
	Tem	0.10	0.25	0.02	-0.32	0.00	1		
	TDS	0.40	0.22	0.30	1	0.50	-0.32	1	
	Nitrate	0.09	0.06	-0.34	0.228	0.28	0.19	0.22	1

### Hierarchical cluster analysis (HCA)

Hierarchical clustering analysis using as several clusters as there are items. Components are increasingly divided into clusters, with the final cluster containing all of the objects. 2 items or a single item and a single cluster or multiple clusters are combined in each phase. The 2 items with the greatest similarity are combined in the first stage. The 2 closest comparable clusters are then combined within each stage. The importance of their similarity (or distance) is preserved. It will be utilized to create the dendrogram, which is a common consequence of these procedures and a dendrogram is a graphical demonstration of the clusters [50].

In the present study, HCA was used to categories samples based on their groundwater quality similarities and to find links between groundwater quality factors. While the HCA results are presented by dendrograms in Figures 4–6. Figure 4 shows the dendrogram of the HP water samples, Figure 5 shows the dendrogram of BH water samples while Figure 6 shows the dendrogram of TW water samples from the study district.

Figure 4 represents the HP dendrogram, which is showing 6 short clusters, 2 medium and two large

clusters. Short cluster contains 6 parameters (WT, Nitrate, Temperature, DO, pH and WSD), mediums cluster contains EC and TDS parameter as illustrated in Figure 4. Figure 5 represents BH dendrogram, it has 6 short clusters, 2 medium and two large clusters. Short cluster contains 6 parameters (DO, Nitrate, WT, pH, Temperature and WSD), mediums cluster contains EC and TDS parameter as shown in Figure 5 below. While Figure 6 representing TW dendrogram it has 5 short clusters, 4 medium and two large clusters. Short cluster contains 5 parameters (Temp, Nitrate, pH, DO and WT) mediums cluster contains EC, TDS and WSD parameter as shown in Figure 5 below.

### Conclusion

The main purposes of this present research work were to know the physicochemical and nitrates toxicity limits and concentration of certain contaminants, TDS, pH, EC, DO and  $\text{NO}_3^-$  in the collected groundwater samples from different water sources like HP, BH and TW from the research zone. The utilization of GIS to analyses the information from the DI Khan district parameter has also

**Table 4.** Correlation matrix of TW water samples in DI Khan.

		WT	WSD	pH	EC	DO	Tem	TDS	Nitrate
Tube wells	WT	1							
	WSD	0.06	1						
	pH	-0.30	0.44	1					
	EC	0.14	0.41	-0.50	1				
	DO	-0.30	0.35	0.75	-0.30	1			
	Tem	0.24	0.29	-0.25	0.18	-0.07	1		
	TDS	0.14	0.41	-0.50	1	-0.30	0.18	1	
	Nitrate	0.23	-0.42	-0.33	-0.28	-0.50	-0.09	-0.28	1



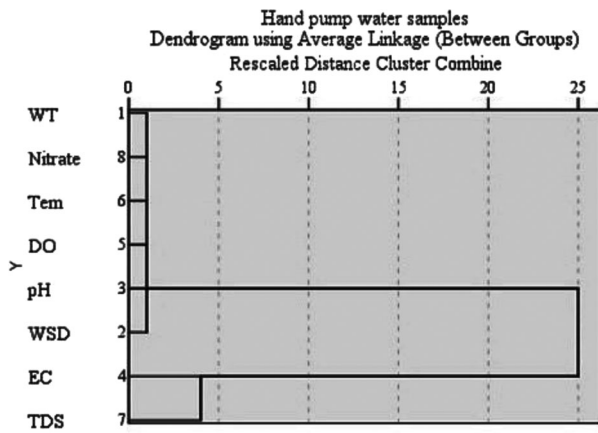


Figure 4. HCA dendrogram of HP water parameters.

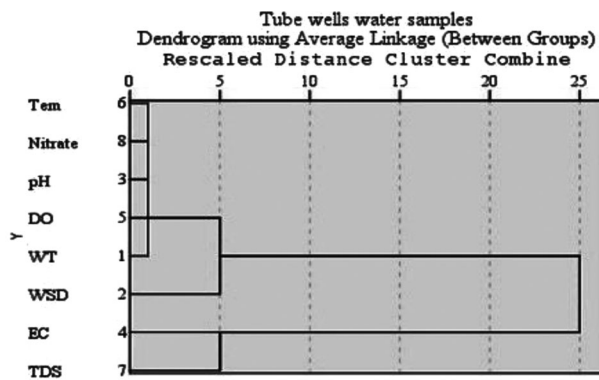


Figure 5. HCA dendrogram of BH water parameters.

proven that to be a much effective technique for assessing the research area. In the study, zone groundwater is critical to fulfilling the local requirement of the population. HP, BH and TW water has been discovered to contain  $\text{NO}_3^-$  a level above  $50 \text{ mgL}^{-1}$ . The concentration of the  $\text{NO}_3^-$  was not within the permissible limit. This can be increased much more the level in humans, plants and animals. The key relation of the groundwater at just the level of the HP

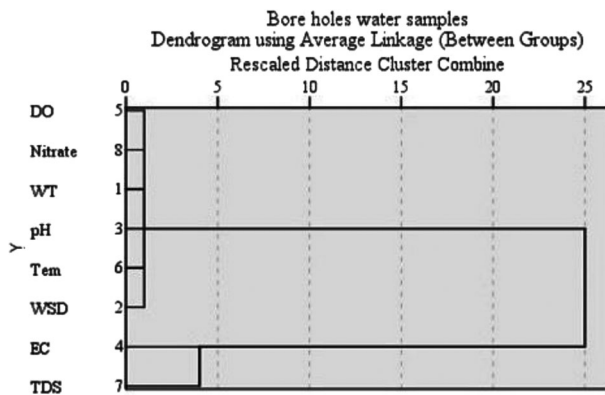


Figure 6. HCA dendrogram of TW water parameters.

samples EC and TDS ( $r = 1$ ) have great correlation, while all other parameters correlations are lower ( $r = 0.40$ ), BH's parameters correlation between WT and WSD ( $r = 0.57$ ), WT and pH ( $r = 0.57$ ), EC and DO ( $r = 0.50$ ), DO and TDS ( $r = 0.50$ ), EC and TDS ( $r = 1$ ) had a higher correlation, while all other parameters correlations were lower ( $r = 0.40$ ). On the other hand, tube well parameters between TDS and EC ( $r = 1$ ) had a perfect correlation, DO and pH ( $r = 0.75$ ) had also a high correlation while all other parameters correlations were less than ( $r = 0.40$ ). To understand more the quantities of physicochemical and  $\text{NO}_3^-$  in plants humans and animals, as well as their impact on their health more research, is needed. All samples studied were successfully correlated using the Pearson correlation coefficient ( $r$ ) approach. The findings demonstrate that crucial water sample metrics like electrical conductivity and total dissolved solids have a perfect positive relationship with one another. While other parameters have a strong positive, moderately positive, and even a significant negative link between parameters.

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### Disclosure statement

No potential conflict of interest was reported by the author(s).

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### Data availability statement

All data generated or analysed during this study are included in this published article (and its additional files). Additional data associated with a paper can be found when contacting to authors, thereafter it can be shared. Requests for material should be made to the corresponding authors.

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