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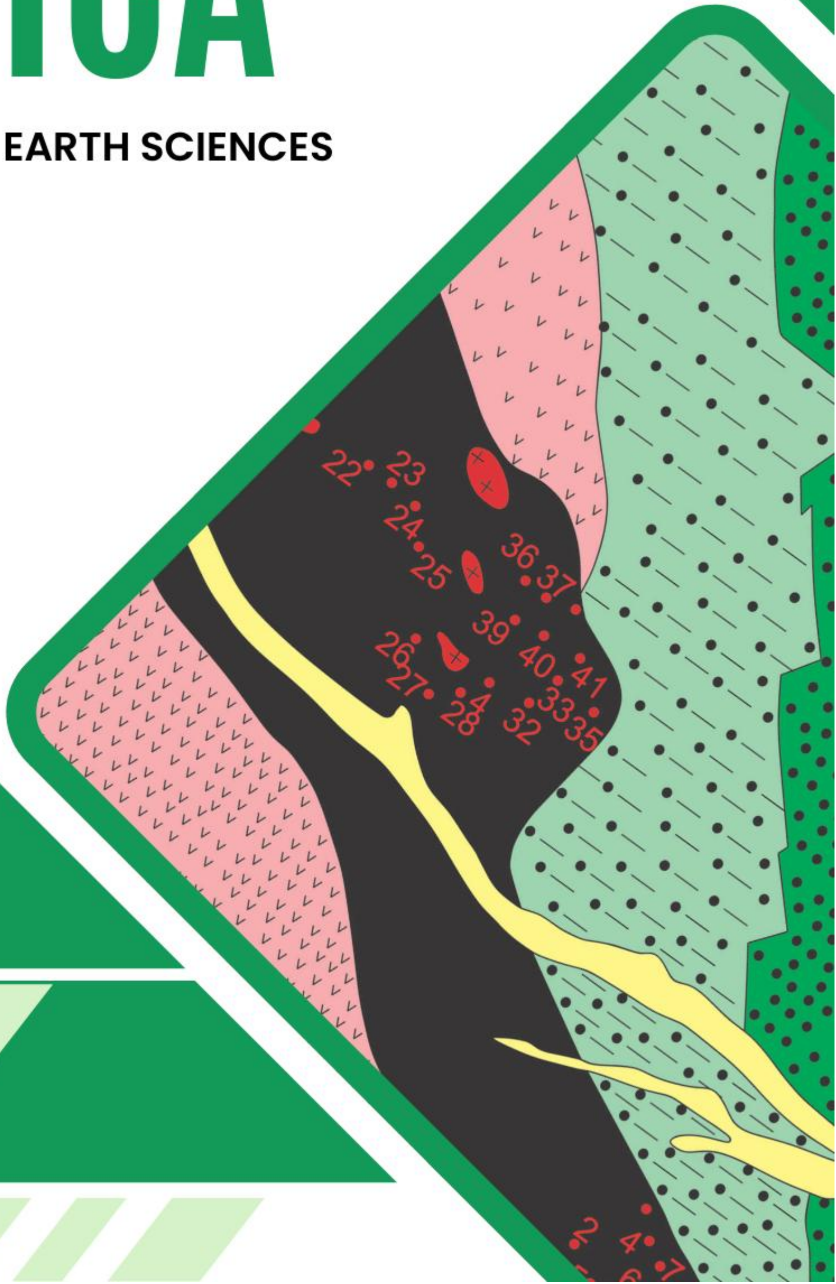

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Spatial Mapping and Health Risk Assessment of Potential Hazardous Elements in Groundwater Using ArcGIS and Multivariate Statistical Analysis

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Abstract

Faisalabad is one of the biggest industrial cities in Pakistan but drinking water quality is declining day-by-day. In the present study a total of 92 samples including drinking water samples, industrial wastewater samples and soil samples along the sewage drains of Faisalabad city and surrounding region were collected from different sampling points. The pH, total dissolved substances (TDS)and conductivity of the samples were 7.9, 2153 ppm and 2847 µS, respectively. The concentration of Pb ranges from 5.16 ppm to 34 ppm with an average concentration of 15.4 ppm while the concentration of As ranges from 8.09 ppm to 54.4 ppm with an average concentration of 17.24 ppm The concentration of Cr ranges from 7 ppm to 140 ppm with an average concentration of 46.8 ppm. The average concentrations of Na^+, K^+, Ca^{2+} and Mg^{2+} were found to be 768.5 ppm, 38.7 ppm, 62.4 ppm and 91.5 ppm respectively. Sodium ion was the major cation while the chloride ion was the major anion making the Faisalabad water undesirable for drinking and domestic purposes. The type of water in such alluvial aquifers is mostly sodium chloride, sodium sulfate and magnesium bicarbonate.

Keywords: Physicochemical parameters, Drinking water, Heavy metal ions, Water pollution

1. Introduction

The scarcity of water is the utmost task in the environmental challenges faced by the arid and semi-arid areas worldwide. The groundwater is a most valuable resource of nature drinkable water for humans over the years but over exploitation of the natural water resources is a threat to the future generation [1, 2]. Since water is a universal solvent and has good fluidity, it is quite likely to be contaminated through different ways. The press statement from the UNO Secretary General on World Water Day in 2002 may be used to understand the significance of having access to good quality drinking water. “An estimated 1.1 billion people lack access to safe drinking water, 2.5 billion people has no access to proper sanitation, and more than 5 million people die each year from water-related diseases which is 10 times the number of peoples killed in wars each year. The two third of the world's population is living in countries which will have moderate or severe water shortages by 2025 [3]. The most important supply of fresh water for consumption, agriculture, industry, and other economic sectors comes from groundwater [4, 5]. Only 0.01% of the freshwater on Earth, which is just 3% of the total global water, is considered as a suitable drinking water source for human [6]. The freshwater content is quickly declining as a result of urbanization, rapid population growth, and unsustainable water usage in agriculture and industry [7, 8]. In the last few decades, there has been gradual deterioration in the purity of groundwater because of many factors such as the rapid population growth, the agricultural activities, the urbanization and industrialization etc. that can contaminate groundwater resource [9]. The rapid deterioration of the environment (soil, water, air)must be consider highly important issue for the research community globally because that can have a direct or indirect effect on human health and wellbeing [10]. Arsenic, mercury, cadmium, and other heavy metals and metalloids have garnered a lot of interest since they are found in many different parts of the environment, including drinking water supplies. These metal ions can seriously damage the liver, kidney, digestive system, and nerve system of humans [11-14]. Considering environmental pollution, many conventions and treaties have been put in place to combat environmental degradation and minimize its associated impact. However, pollution levels continue to rise in every component of the environment. Groundwater is the base of livelihood, and its pollution has emerged as one of the prime and rapidly increasing environmental hazard [15].

Among various factors, the weathering of rocks is the primary factor contributing to a large amount of soluble salts in ground water [16]. Heavy metal ions contaminating ground water comes from different rock types. These rocks originate from magma cooling which is composed of different elements including heady metal ions such lead, arsenic and cadmium *etc* [17]. The ground water passing through the igneous rocks can dissolve small quantities of minerals [18]. Different practices such as leakage from underground storage tanks, sewage systems, salt-water intrusion, harsh agriculture practices, snow removal with salt on highways *etc*. can contaminate ground water landfills [19, 20]. Given their fluctuating climate, growing population, and finite freshwater supply, it is extremely difficult to comprehend the geochemistry of a region in order to protect groundwater reserves [1]. Understanding the chemistry and composition of groundwater requires an knowledge of hydrochemistry [2]. Aquifer lithology, recharge of groundwater, aquifer-water interactions, and human activity are some of the natural forces that affect the composition of trace elements in groundwater [4]. Furthermore, in order to properly interpret the findings from a certain study region, suitable statistical techniques are also used to identify the temporal and spatial trends [5]. Groundwater element spatial analysis, backed by suitable geostatistical methodologies, is well documented in the literature [21].

The polluted water could affect a person's ability to operate normally, the person is mentally affected from the heavy metals [22]. Presently, agricultural and industrial chemical waste disposal are among the main causes of water pollution [23]. In many parts of the world, there is a significant issue with the release of soluble arsenic materials into the ground water [24-29]. Toxic metals must be effectively removed from water for people and other living things to survive. A number of techniques have been developed to remove metal ions from water, including chemical precipitation, membrane filtration, reverse osmosis, solvent extraction, and flotation [30]. Nanotechnology has been extensively used to developed new methods and materials for efficient water treatment [31].

The current study emphasizes one of the main public health concerns: the health risks associated with exposure to heavy metals from drinking groundwater. Assessing health risk aids in determining the hazardous environmental risk sources and calculating the quantity of risk agents that expose people to and maintain their health. Multivariate statistical analysis is used to identify the source of contaminants, and ArcGIS is used to analyse the heavy metals' spatial distribution.

2. Experimental

2.1 Study Area

Faisalabad is bordered to the north by Gujranwala and Sheikhupura districts, to the east by Sahiwal district, to the south by Toba Tek Singh district, and to the west by Jhang district. The city is known as the Manchester of Pakistan because several industries are in this district, that’s why study area is selected for the groundwater research. It is Pakistan's third-largest district, southwest of Lahore in the middle of Punjab province and sits this significant industrial hub. Faisalabad is known as the "city of textiles". The typical high and low temperatures throughout the summer are 39 °C (102 °F) and 27 °C (81 °F), respectively. Figure 1shows the location map of the study area.

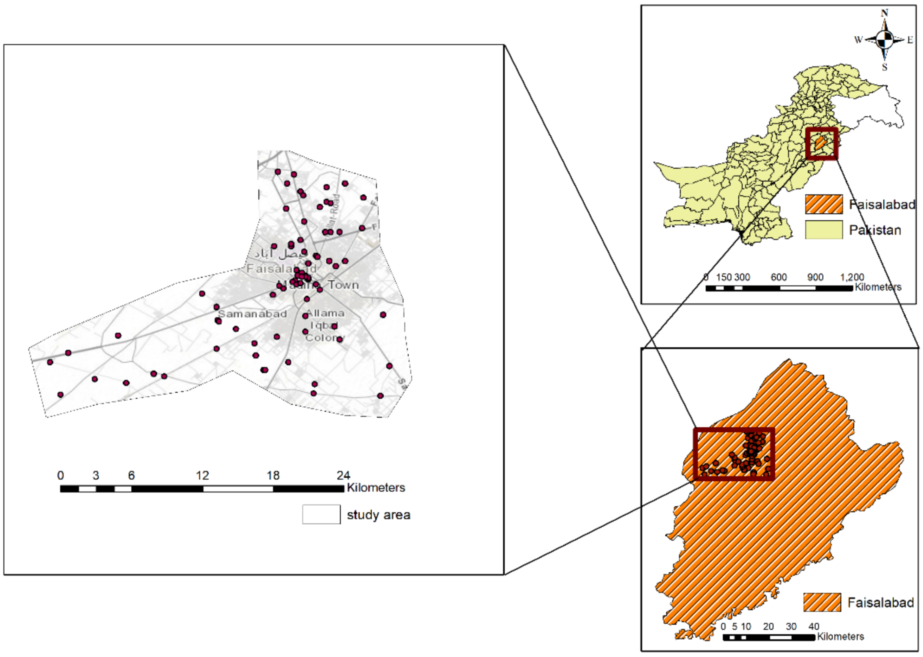

Figure 1. Graphics showing the study area and location of sampling.

2.2 Ground-Water Sampling

A total of 92 drinking water samples were collected from different locations (Figure 2) to study the number of different contaminants and their correlation with each other. The ground water samples were taken from tube wells, hand pumps and donkey pumps at different depths in propylene bottles. The physicochemical parameters were calculated using portable pH meter, TDS meter and Electrical conductivity meter during sample collection. The chemical laboratory where heavy metals were analyzed was located far from the study area; therefore, physicochemical parameters were analyzed using portable devices as microorganisms are incorporated into the samples which may change the results of pH, TDS and Electrical Conductivity. For Atomic Absorption Spectroscopic analysis, the samples were prepared according to EPA methodology, the water samples were boiled slowly to evaporate lowest possible volume, later 5 ml of concentrated nitric acid was added. The samples were evaporated again to dryness and the beakers were cooled, followed by addition of 5 ml of HCl solution (1:1 v/v). All the solutions were warmed later 5 ml of 5 M NaOH was added and finely filtered [32].

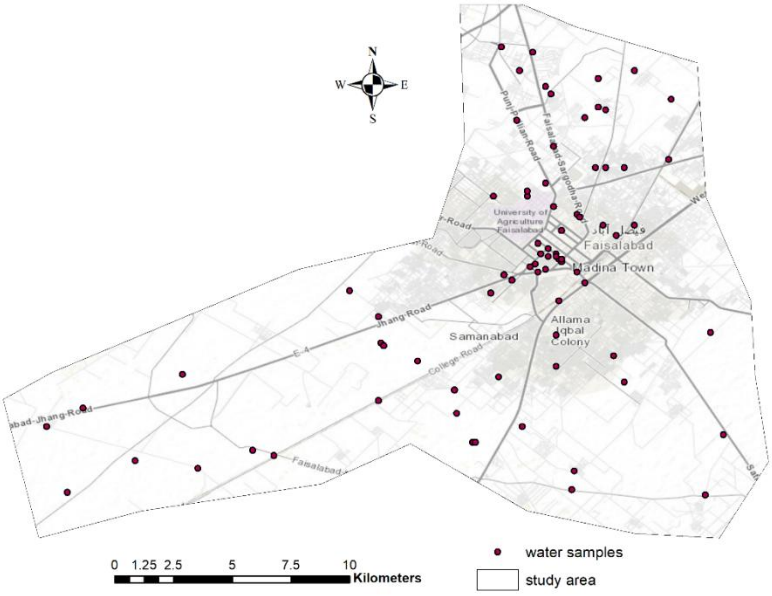

Figure 2. Map showing the locations of sampling in the study area.

2.3 Physical and Chemical Characterization

The technique of acid-base titration was used to evaluate the HCO_3^-, and suppressor-type ion chromatography (Metrohm 861 Advanced Compact IC) was used to investigate the other anions (SO_4^-, F^-, and Cl^-). A portable electrode (HORIBA D-54) was used to measure the pH, TDS, and electrical conductivity (EC).

The cations were analyzed using AAS Perkin Elmer 800. The instrument AAS was calibrated using standard solution of each respective element. For ppm range the standard solutions of various concentrations 0.5, 1, 2, 4, 8 and 16 ppm from stock solution of 100 ppm while for ppb range the standard solutions of 5, 10, 20, and 40 ppb from stock solution of 100 ppb were prepared.

2.4 Statistical Analysis

To determine the relationship between the content of metallic elements and their origins in ground water, descriptive statistical analysis was used. Using SPSS 19, the multivariate statistical analysis included principal component analysis (PCA) and cluster analysis (CA). The Ward's approach was used to classify the data after it was normalized on the Z-score (mean = 0 and standard variation = 1) [30].

2.5 Geochemical Mapping

Spatial analysis was conducted using ArcGIS 10.5 software; IDW interpolation was utilized, which precisely permits thorough spatial variation of the data [4]. The spatial distribution of heavy metals from the sample locations was shown by the geochemical maps by pointing out the hotspots of the area and the status of pollution in the area was interpreted [21].

3. Results and Discussion

3.1 Physical Parameters of Ground-Water

In the drinking water of the study area, the pH ranges from 6.98 to 8.96 with an average of 7.94 while the TDS ranges from 389 ppm to 5711 ppm. The conductivity was found to be 450 μS to 7600 μS. The spatial maps show the levels of pH, TDS and conductivity as can be seen below in Figure 3.

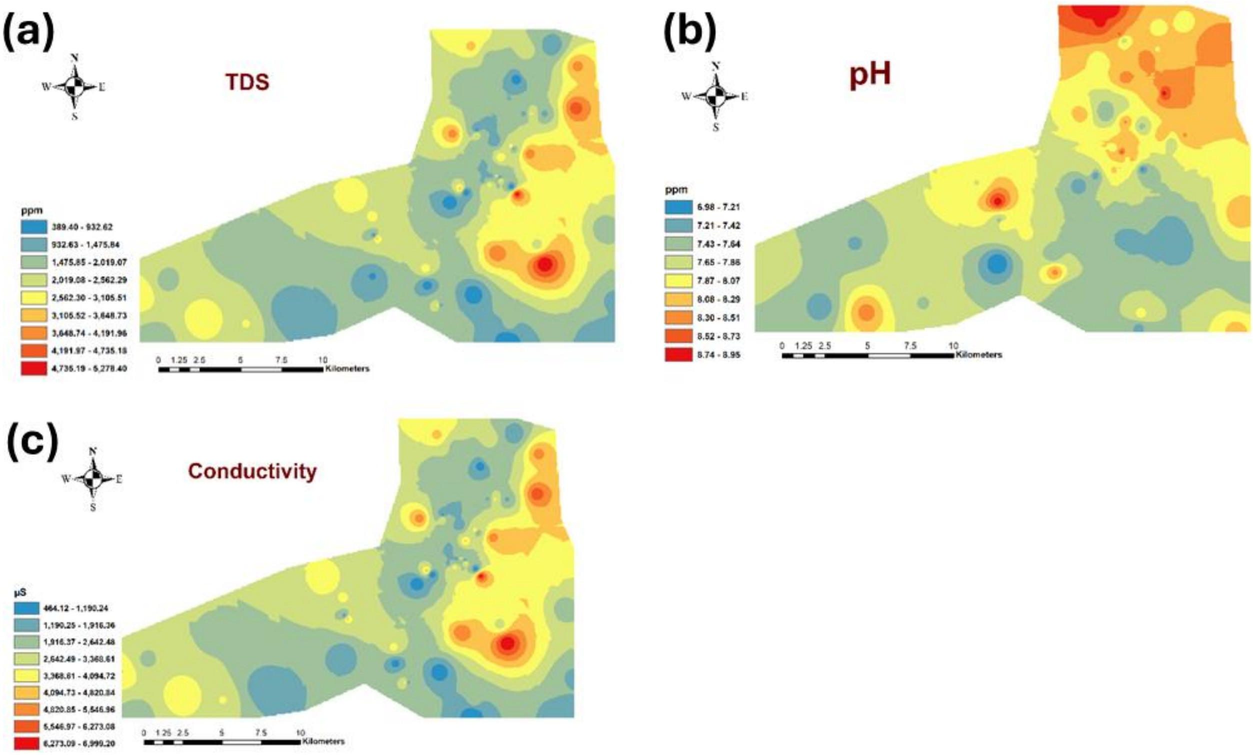

Figure 3. Water quality spatial maps of study area (a) TDS, (b) pH and (c) Conductivity

3.2 Metal Concentrations

The metal concentrations of elements along with the statistical parameters are shown in Table 1. The concentration of Pb ranged from 5.20 ppm to 34.0 ppm with an average concentration of 15.4 ppm while the concentration of As ranged from 8.10 ppm to 54.4 ppm. The concentration of Cr ranges from 7 ppm to 140 ppm with an average value of 46.8 ppm. The average concentrations of Na^{+}, K^{+}, Ca^{+2} and Mg^{+2} were found to be 769 ppm, 38.7 ppm, 62.4 ppm and 91.5 ppm respectively.

Table 1. Concentration (ppm) of different elements in the study area

	Na	K	Ca	Mg	As	Pb	Cr
Mean	769	38.7	62.4	91.5	17.2	15.4	46.8
Median	689	27.5	54.5	69.5	14.7	13.9	44.0
Min	60.0	2.65	1.62	4.00	8.09	5.16	7.00
Max	2314	147.0	325.0	204	54.4	34.0	140

Range	2254	144.3	323.4	200	46.3	28.9	133
SD	520.5	28.5	42.3	68.6	9.76	7.50	31.4
RSD	67.7	73.6	67.7	75.0	56.6	48.6	67.0
Skewness	0.64	1.66	3.00	0.23	2.56	2.10	1.10
Kurtosis	-0.20	2.76	16.0	-1.64	7.66	4.78	1.28
p (S-W test)	0.01	0.68	0.42	0.00	0.00	0.00	0.00

p-Values of Shapiro-Wilk test for normality of the raw data. For values greater than 0.05 distribution is normal.

3.3 Anionic concentrations

The concentrations of anions including bicarbonates, sulphates, fluorides and chlorides are given in Table 2. It is shown that the concentration of fluoride ion ranges from 0.13 ppm to 2.61 ppm while that of chloride ranges from 75.00 ppm to 2201 ppm. The average concentration of bicarbonate and sulphates was found to be 365.95 ppm and 154.45 ppm respectively.

Table 2. Concentration (ppm) of different anions in the study area

	HCO_3^-	SO_4^{-2}	F^-	Cl^-
Mean	366	154.5	0.84	668.7
Median	318	120.5	0.67	583
Min	89.0	14.0	0.13	75.0
Max	915	574	2.61	2201
Range	826	560	2.48	2126
SD	195.8	105.6	0.60	457.2
RSD	53.5	68.4	71.2	68.4
Skewness	0.93	1.53	1.32	0.93
Kurtosis	0.19	2.73	0.92	0.96

3.4 Hydrological Character of Study Area

The district of Faisalabad is located on the alluvial plains that lie between the centre of the Indian subcontinent and the foothills of the Himalayas. The alluvial deposit has a thickness of over a thousand feet and can reach several thousand feet in certain locations. Plains comprise of the early Holocene deposits of the Ravi and Chenab River and occupy a major part of Kamalia Tehsil and small part of Chenab plains. The soil comprises young stratified silt loams or very fine sandy loam having a weak subsoil structure with common cankers within five feet depth [31].

3.5 Metal Clustering and Correlations

A higher correlation between metal ion concentrations indicates a shared source in the area under study, according to the Pearson correlation analysis, which offers information on metals and their origin. Strong relationships between Ca^{2+}, Na^+, Mg^{2+}, and K^+ were revealed by the Pearson correlation, as indicated in Table 3 (Na–K 0.651, Ca–K 0.339 and Na–Ca 0.309). Next close relationship was found among Cr, Pb, and As which is As–Cr 0.295 and As–Pb 0.248. Both the alkali metal ions (Na^+, K^+, Ca^{2+} and Mg^{2+}) and heavy metal ions (Cr, Pb and As) groups have negative correlation with one another indicating different sources.

Table 3. Pearson Correlation matrix of studied elements in the groundwater samples

	As	Ca	Cr	K	Mg	Na	Pb
As	1.00	0.14	0.20	-0.01	0.14	0.09	0.25
Ca	0.14	1.00	0.27	0.34	0.22	0.31	-0.02
Cr	0.29	0.27	1.00	0.08	0.02	0.02	-0.05
K	-0.01	0.34	0.08	1.00	0.23	0.65	-0.12
Mg	0.14	0.22	0.02	0.23	1.00	0.27	-0.16
Na	0.09	0.31	0.02	0.65	0.27	1.00	-0.18
Pb	0.25	-0.02	-0.05	-0.12	-0.16	-0.18	1.00

Correlation is significant at the 0.01 level (2-tailed).
Correlation is significant at the 0.05 level (2-tailed).

The correlation between the metals in two clusters is confirmed by the hierarchical cluster analysis using Ward's approach [30], which also tracks the natural and man-made sources of these metal ion concentrations. The Ca^{2+}, Na^{+}, Mg^{2+}, and K^{+} make up the first cluster, whereas As, Cr, and Pb make up the second (Figure 4). The hierarchical dendrogram results are in line with the Pearson correlation data (Table 5), which indicates that whereas Ca^{2+}, Na^{+}, Mg^{2+}, and K^{+} originate naturally, As, Cr, and Pb originate anthropogenically.

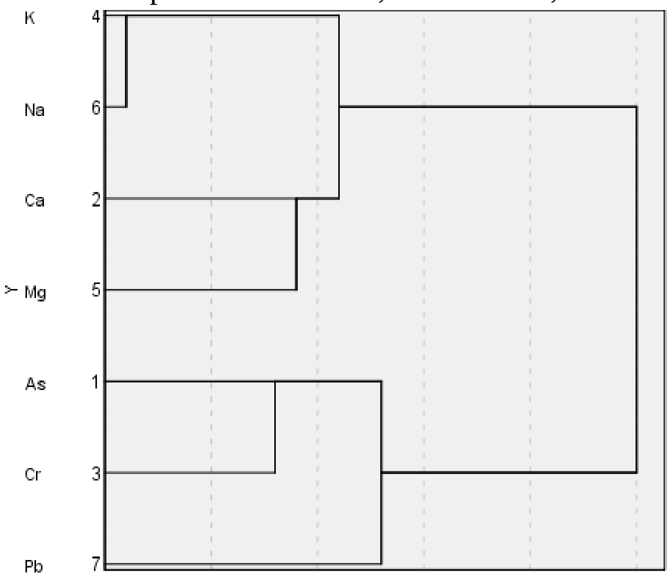

Figure 4. Hierarchical dendrogram for the metal ions (Ward's method)

3.6 Principal component analysis

When Eigen value is greater than 1 with varimax rotation with Kaiser Normalization, factor extraction was studied using principal component analysis (PCA). Extracted factors explain variance and principal component (PC) loadings aid in interpreting. To find out where the constituents in ground water came from, PCA was used. Kaiser-Meyer-Olkin (KMO) and Bartlett's test of sphericity were employed to assess the appropriateness of the sampling. The findings of KMO (0.70) and Bartlett's test ($p<0.001$) verified that

PCA was appropriate for the dataset. The PCA data for all the elements from 92 different samples are shown in Table 6.

Table 6. Total variance explained for heavy metal contents

Component	Initial Eigenvalues			Extraction Sums of Squared Loadings			Rotation Sums of Squared Loadings		
	Total	Variance (%)	Cumulative (%)	Total	Variance (%)	Cumulative (%)	Total	Variance (%)	Cumulative (%)
1	2.16	30.9	30.9	2.16	30.9	30.9	2.13	30.4	30.4
2	1.42	20.2	51.1	1.42	20.2	51.1	1.45	20.7	51.1
3	0.99	14.2	65.3						
4	0.89	12.7	78.0						
5	0.71	10.2	88.2						
6	0.51	7.29	95.5						
7	0.32	4.51	100						

It is evident that three main components with cumulative variance of 51.1 % and eigenvalues greater than one are taken out of the data set. High PC loadings for Ca^{2+}, Na^{+}, Mg^{2+}, and K^{+} are shown by the first PC's percentage variance of 30.9 %, whereas the second PC's variance is 20.2 %. Figure 5 displays the PC loadings plot. When two clusters were divided by the identical element groups, the PCA showed perfect agreement with the cluster analysis.

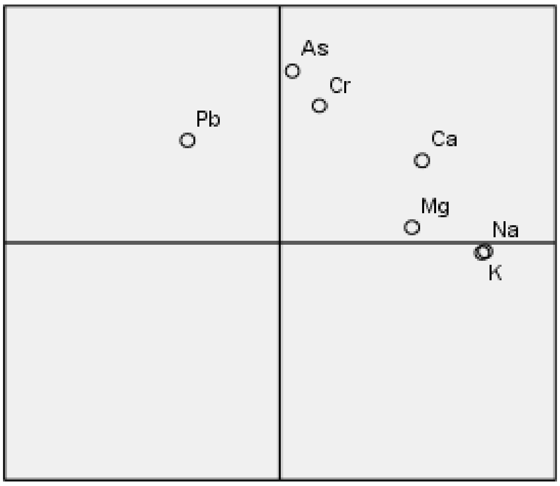

Figure 5. Principal loadings of the three principal components after varimax rotation

3.7 Correlation of Cationic Concentrations with the Anionic Concentrations

The ground water has a positive correlation of Na^{+} and Cl^{-} ions as shown in Figure 4. The high concentration of NaCl is the saline character of the groundwater. The higher concentrations of Na^{+} and Cl^{-} ions in groundwater indicate the geological setting, industrial effluent and domestic waste. The chemistry between the K^{+} and Cl^{-} ions is negative as compared to Na^{+} and Cl^{-} correlation. The correlation of Ca^{+2} with sulphates is weak and not very positive. The chemistry of ground water reflects that the correlation between the Mg^{+2} and sulphates is positive but not too strong as the chemistry of Na^{+} and Cl^{-}. The chemistry of ground water also reflects that type of water is Ca^{+2} and Mg^{+2} sulphates type. A positive correlation between Ca^{+2} and bicarbonate also show that the type of water in Faisalabad is saline as well as hard and has alkaline pH. The graph shows that there is a positive correlation between Na^{+} and sulphate. There are numerous potential causes for ground water pollution caused by chromium ions. In the Faisalabad District Ravi and River Chenab, the chloride ion concentration is less than 100 $mgL^{-1}$of the aquifer. The alluvial aquifer's water often contains sodium chloride and calcium bicarbonate.

3.8 Mapping and Spatial Analysis

The spatial distribution of elements pointed out the areas with high concentration and lower concentrations shown in Figure 5. The spatial map of As shows the maximum concentration at the rural areas of Faisalabad indicating the natural abundance of the elements while the other elements are randomly distributed in the study area. The Pb is also found in the urban areas of the Faisalabad which is an anthropogenic contribution by the domestic and industrial use.

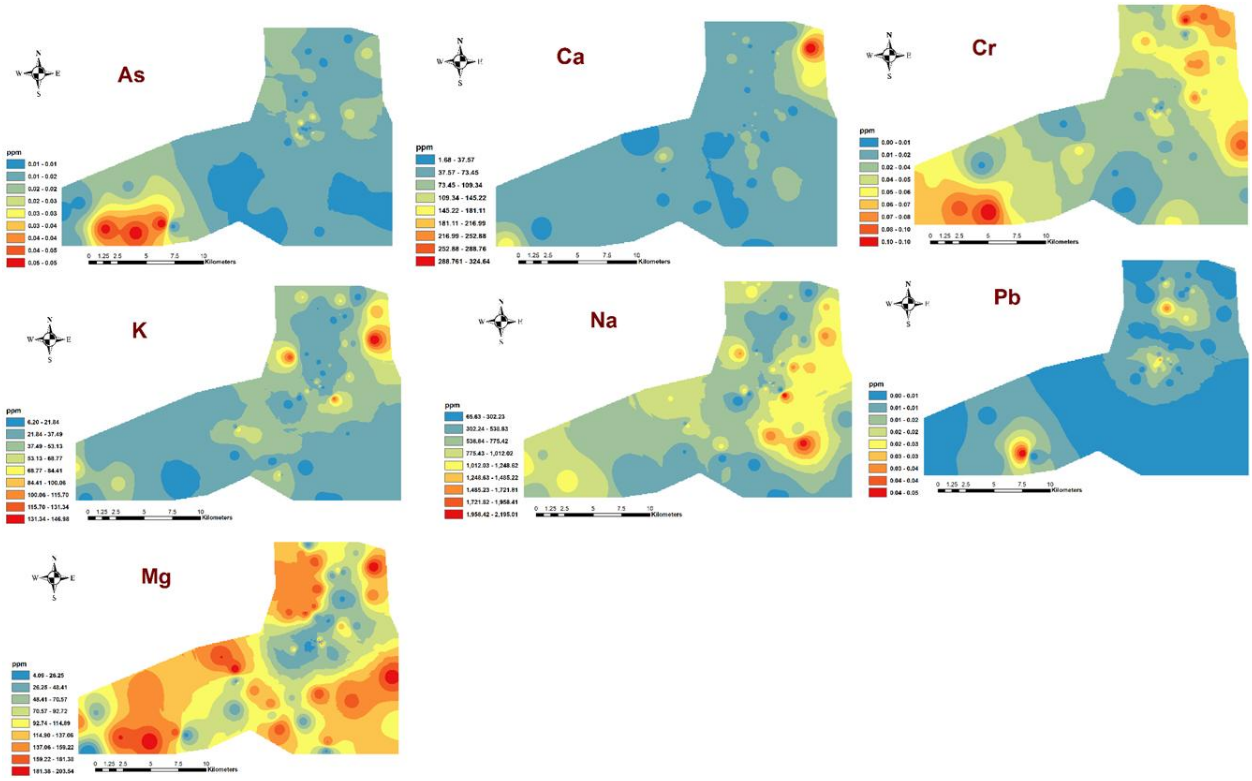

Figure 5. Spatial distribution of different elements in the study area

The spatial maps of anionic concentrations of bicarbonates, sulphates, fluorides and chlorides are shown in Figure 6. The maps indicate the clear picture of distribution of anions in the study area with different concentrations which is also defined by the positive and negative correlation with the concentration of elements.

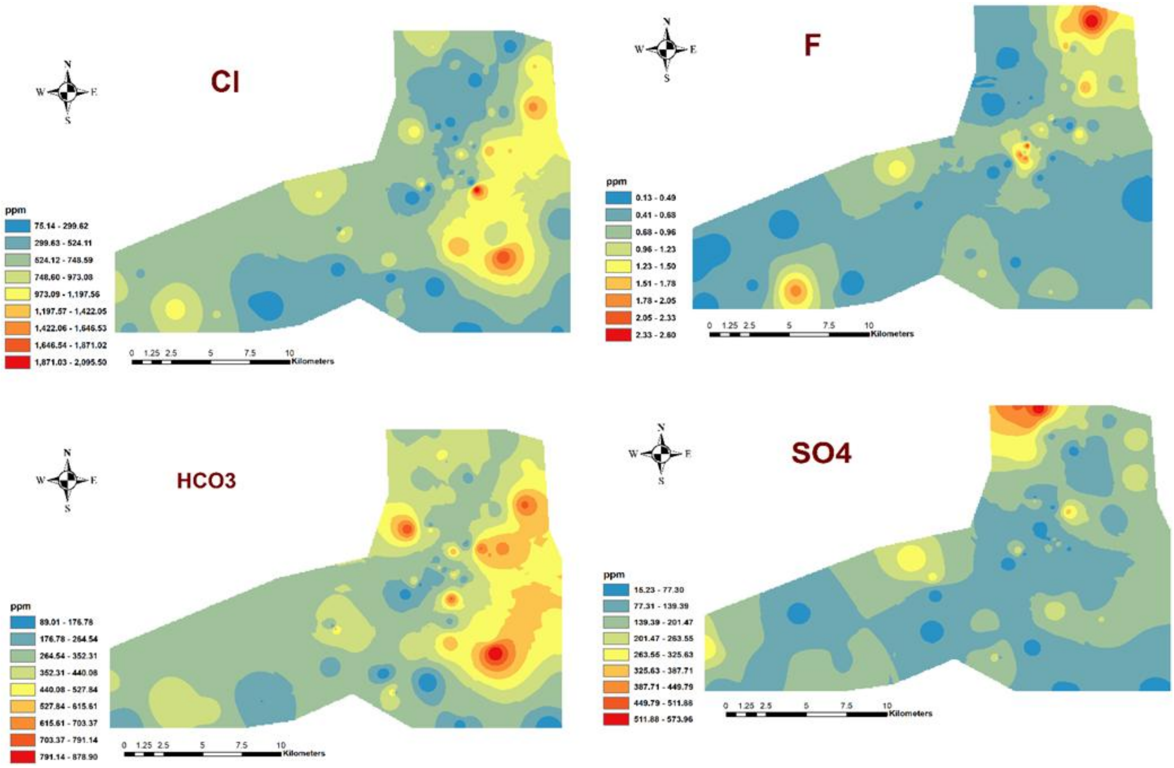

Figure 6. Spatial distribution of different anions in the study area

4. Conclusion

The quality of groundwater was determined in Faisalabad City Pakistan. The high concentration levels of arsenic, lead, and chromium were observed along with the higher concentrations of carbonates, sulphates, chlorides and fluorides. Due to the precipitation of carbonate minerals and cation exchange process, the levels of Na^{+}, Ca^{2+} and Mg^{2+} are often low. Lower Ca^{2+} concentrations can accelerate the dissolution of F^{-} whose concentration is regulated by fluorite's solubility. Due to the significant percentages of sulfates, bicarbonates, chlorides and fluorides in groundwater, the conductance and total dissolved solids are quite high. The shallower portions of the aquifer between 20 and 30 meters were deep, although the ground fluids are conveniently divided into three levels, they are likely related, and contaminants may move into the deeper portion of the same reservoir. The dangerous risks of drinking straight from boreholes should be communicated to the local population. Health risks may be communicated to the authorities, who would then attempt to provide drinkable water.

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Credit author statement

Dr. Syed Ishtiaq Khan: Conceptualization, Methodology, Data Curation, Khadim Hussain Rajper: Investigation, Methodology, Data curation, Ali Qasim: Conceptualization, Methodology, Data Curation, Dr. Raja Karim Bux: Investigation, Methodology, Data curation, Writing- Reviewing and editing draft preparation, Sania Gul: Conceptualization, Methodology, Data Curation.

Conflict of interest

The authors declare that there is no known conflict of interest for competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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