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Original Research

Human Health Risk Assessment and Source Identification of Toxic Heavy Metals by Multivariate Tools in Groundwater

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Abstract

Groundwater contamination is a major threat to people depending on groundwater for their daily water supply. The quality of groundwater has degraded due to the release of toxic contaminants in groundwater from natural as well as man-made practices, thus resulting in the spread of water-related diseases to humans. Thus, this study was planned to assess the groundwater contaminants and their associated health effects on the residents of Lahore City, Pakistan. To assess the physicochemical properties of groundwater, randomly, 62 samples of groundwater were collected from all over the study area. The data showed that the Electrical Conductivity (EC), Total Dissolved Solids (TDS), pH, and sulfates exceeded the safe limit of the National Environmental Quality Standards (NEQS), and the concentration of heavy metals (lead, chromium, and cadmium) was also much higher than the NEQS and World Health Organization (WHO) recommended levels. The multivariate analysis, such as Principal Component Analysis (PCA) and cluster analysis, confirmed that toxic heavy metals, including lead, chromium, and cadmium, originated from similar sources, such as industrial activities in the study area. The results from chronic daily intake, hazard quotient, and cancer risk also demonstrated that lead, chromium, and cadmium tested heavy metals showed potential carcinogenic and non-carcinogenic risks to children and adults in the study area. Thus, this study concluded that

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groundwater is highly contaminated and not fit for human consumption. Future studies are required for constant monitoring of groundwater quality and to develop mitigation methods to improve its quality on urgent basis.

Keywords: carcinogenic, health risk, heavy metals, water

Introduction

Groundwater is known as a precious asset since the economies of the countries in the world are dependent on groundwater resources. Water scarcity has impacted >3 billion individuals in the last 2 decades. A large range of toxic chemicals released from anthropogenic activities are responsible for the pollution of groundwater systems [1]. The release of hazardous pollutants from industrial activities, agricultural runoff, and households, including toxic heavy metals, is considered the largest contributor to groundwater pollution on Earth [2]. The absence of proper sanitary options causes these toxic heavy metals to be released into groundwater [3]. Heavy metals with massive toxicity and carcinogenic effects have been examined in previous research works to protect and sustain precious groundwater systems [4] as well as their human health risks [5].

Long-term interactions with different heavy metals through different pathways, for example, cooked food, drinking water, and crop irrigation may lead to direct or indirect heavy metal accumulation in different parts of humans [6], resulting in potential health issues including osteoporosis, respiratory diseases, imbalance of endocrine glands and dermal issues, hypertension, cardiovascular, reproductive, and neurological issues [7].

Although heavy metals are known as one of the major pollutants in groundwater resources, a few metals, including iron and zinc, are regarded as essential metals for the health, growth, and development of living organisms. In contrast, mercury, lead, and cadmium are considered non-essential metals to living organisms owing to their potential toxicity [8].

Heavy metal toxicity depends on their concentration in various sectors of the environment, and they could accumulate significantly in the tissues of living organisms and concentrate via the food chain [9]. Heavy metals such as lead, chromium, cadmium, and copper are a few examples of toxic heavy metals, and if they are consumed beyond the allowable limit, they could cause serious diseases such as high blood pressure, kidney issues, skin problems, and liver cancers.

Safe drinking water is necessary for human health, but nowadays people in Pakistan have very little access to safe drinking water, and as a result, people face a large number of health-related diseases [10]. In Pakistan, only 40% of the population drank drinkable water either extracted from underground sources or rivers, dams, and natural ponds.

Diarrhea, typhoid, cryptosporidium infection, gastro-enteritis, giardiasis, intestinal worms, and hepatitis are different diseases associated with drinking water in Pakistan. In Pakistan, according to the IUCN, 60% of infant deaths have been caused by water-borne diarrhea [11].

Lahore, being the second-greatest city in Pakistan, largely depends on groundwater to fulfill the needs of its citizens, but the groundwater level is presently falling at a disturbing pace of roughly 0.7 to 0.9 m a year. The water table in the city center has gone down by 40 meters and is expected to fall under 70 meters by 2025. Uncontrolled urbanization and industrialization are causing severe problems for public administration, and groundwater is perhaps influenced the most [12]. It has become difficult for the government to manage water supply with the expanding demand. The groundwater consumption in Lahore has increased greatly, but the quality of groundwater as well as surface water has been in danger because of the addition of poisonous pollutants from sewerage, industrial effluents, and the partial removal of untreated modern effluents and rural practices. Untreated modern effluents have been disposed of into streams moving through or nearby living places. The inhabitants living along the channels obtain their drinking water supply from shallow siphons introduced close to the channels. From the above-mentioned facts, it is evident that more studies are required to explore the groundwater quality and human health risk assessment in residential areas of Lahore, Pakistan. A very high chance of contamination of groundwater with heavy metals, primarily due to adjacent industrial zones, persists in Lahore. Also, data linking groundwater contamination in residential areas to industrial activities and resulting human health risks from heavy metal contamination in groundwater is still lacking. Considering the above facts, the current study was planned to (a) analyze groundwater quality parameters of residential areas in Lahore, (b) estimate the source examination of different heavy metals, including cadmium, chromium, and lead using multivariate analysis, and (c) assess possible human health risks of heavy metals from the intake of groundwater.

Experimental

Study Area

The study was conducted in various areas of Lahore, Pakistan. Lahore is a city located between 31°32'59"N and 74°20'37"E (Fig. 1). It is located in the province of Punjab in Pakistan. It is the second-largest city in the country and is known for its rich history, culture, and food. Lahore has a population of over 11 million people and is considered the cultural capital of Pakistan. It is on the banks of the Ravi River, which flows through the city from north to south. The city covers an area of approximately 1,017 square kilometers and is situated at an elevation of 217 meters above sea level. Lahore is bordered by the Indian state of Punjab to the east, the Sheikhupura District to the northwest, the Kasur District to the south, and the Nankana Sahib District to the west. The city is divided into nine administrative towns, each of which is further divided into Union Councils. The climate of Lahore is characterized by hot summers and mild winters, with temperatures ranging from a maximum of 45°C in the summer to a minimum of 0 °C in the winter. The city experiences monsoon rains from July to September, which provide relief from the scorching heat of the summer months. Large seasonal changes in temperature and precipitation are a feature of Lahore. On average, about 575 mm of rainfall is reported for Lahore, which ranges from 300 to 1200 mm.

Sampling and Sample Pre-Treatment

Groundwater samples (*n = 62*) were collected from major areas in Lahore, Pakistan (Fig. 1). In most areas, groundwater is used for domestic purposes such as drinking, cleaning, and bathing. The study area also includes sites where groundwater is also used for irrigation of crops, and they are adjacent to industries as well. For obtaining samples, the tap was opened or switched on motor pumps for approximately 5 minutes before collection of the water sample in order to get fresh water. Water samples obtained from sampling sites were saved in polypropylene bottles, which were pre-washed with HNO_3 (10%) and then carefully washed with distilled water (DW). A part of each sample was acidified using conc. HNO_3 (to avoid precipitation of metal ions) for analysis of metal ion concentration, i.e., lead (Pb), cadmium (Cd), nickel (Ni), copper (Cu), arsenic (As), and chromium (Cr) [13]. Non-acidified water samples were employed for the determination of physic-chemical

Fig. 1. Map of the study area.

properties, i.e., pH, total dissolved solids (TDS), total suspended solids, electrical conductivity (EC), and calcium + magnesium ions (Ca + Mg), as well as anions, i.e., carbonates (CO_3), bicarbonates (HCO_3), chlorides (Cl^-), and sulfates (SO^{-2}_4). All groundwater samples were preserved in the refrigerator at a temperature of 4ºC.

Physiochemical Analysis of a Water Sample

All physico-chemical parameters in this were determined through the standards and formula given elsewhere [13, 14]. The pH, TDS, and EC of water samples were measured using pH/EC/TDS/Salinity Meter 372 (Systronics, China). Sulfate and TSS in water samples were measured by gravimetric analysis, while CO_3, HCO_3, and Cl^- were measured using the titration method as described previously [15, 16].

Analyses of Heavy Metals

The concentration of heavy metals such as Pb, Cr, Cd, As, Cu, and Ni was estimated in acidified water samples using an atomic absorption spectrometer.

Chemicals and Quality Control

For the analyses of different physico-chemical parameters, analytical grade chemicals/reagents were employed. All the standards, reagents, and water samples were prepared or diluted with DW. Working standards solutions were prepared in 5% HNO_3 with ready-made stock standard solutions of different metals. Moreover, double DW was used for instrument cleaning at regular intervals to avoid analyte deposition in the instrument.

Health Risk Assessment

Health Risk Assessment is a method in which the risk estimation is carried out from toxic compounds or metals that accumulate over a long period in humans through drinking water, breathing air, or contact with polluted soil. The health risk assessment of heavy metals showing higher concentrations (Pb, Cd, and Cr) was calculated.

The Chronic Daily Intakes (CDIs) in mg kg^{-1} day^{-1} of Pb, Cd, and Cr through everyday intake of groundwater in humans were analyzed using Eq. (1) as described below [17]:

$$CDI = \frac{CM \ x \ DI}{BW} \quad (1)$$

where CM is the heavy metal concentration (mg L^{-1}) and DI shows the Daily Intake of water (3.45 L day^{-1} for adults while 2 L day^{-1} for children) [18]. While BW represents average Body Weight, which is assumed to be 73 kg for adults and 32.7 kg for children.

The hazard quotient (HQ) value owing to a daily intake of drinking water contaminated with heavy metals was obtained by Eq. (2):

$$HQ = \frac{CDI}{R_f D} \quad (2)$$

where R_fD describes Oral reference doses, which were 0.003 and 0.0005 for Cr and Cd, respectively, in mg $kg^{-1}day^{-1}$ [19]. For Pb, no RfD value has been set by USEPA; hence, HQ values were not obtained for Pb.

Cancer risk (CR) of exposure to heavy metal contaminated water was measured for Pb, Cr, and Cd using Eq. (3) [14]:

$$CR = CDI \ x \ CSF \quad (3)$$

where CSF represents the Cancer Slope Factor, which is the risk from specific heavy metals. The values of CSF for Cr are 0.5, while for Pb and Cd, CSF values have not been prescribed by USEPA, thus no CR was performed for Pb and Cd.

Results and Discussion

Physico-Chemical Analysis

Results of the physico-chemical analysis of groundwater samples are presented in Table 1. Groundwater samples (n = 62) were found slightly alkaline (pH = 7.89) with an average EC of 1360 µS cm^{-1}. This EC value was found within the permissible limit of the World Health Organization (WHO) (2000 µS cm^{-1}) in most of the water samples but higher than the Water Recourses Control Board, California (900 µS cm^{-1}) [20]. A higher TDS value was noted (671.3 mg L^{-1}) as compared to the WHO (≤300 mg L^{-1}) recommendation however, considered safe as compared to the Pakistan Environmental Protection Agency (Pak–EPA) limit (<1000 mg L^{-1}). These parameters are indicating the high concentration of dissolved ions in collected samples of the study area. Total suspended solids (TSS) were also found relatively higher (486.226 mg L^{-1}) in water samples (Table 1). This could be due to high anthropogenic activities because dissolved pollutants can attach to suspended water particles and decrease water quality [21].

The mean contents of CO_3 (1.381 mg L^{-1}), HCO_3 (4.535 mg L^{-1}), SO_4 (5.197 mg L^{-1}) and were found within the acceptable limits of the WHO and Pak–EPA. However, higher Cl (935.31 mg L^{-1}) contents were found in groundwater samples as compared to both WHO and Pak-EPA limits (250 mg L^{-1}) (Table 1). The mean value of Ca + Mg was 5.76 mg L^{-1} in the study area. This could be attributed to the high dissolution of Cl salts from parent rocks and industrial activities (especially in the Lahore region) into the groundwater table [21].

Table 1. Concentration of heavy metals and other groundwater quality parameters and maximum permissible limits set by World Health Organization (WHO) and Pakistan Environmental Protection Agency (Pak-EPA).

Parameter	Range	Mean	S.D (±)	Median	WHO safe limit[a]	Pak-EPA safe limit[b]
pH	7.3-8.9	7.895	0.335	7.85	6.5-8.5	6.5-8.5
EC (µS cm^{-1})	280-2780	1360	703.858	1135	2000	-
TDS (mg L^{-1})	150-1360	671.306	343.244	595	≤300	<1000
TSS (mg L^{-1})	247-913	486.226	195.448	410	-	-
CO_3 (mg L^{-1})	0-3.1	1.381	0.929	1.6	500	-
HCO_3 (mg L^{-1})	2-10	4.535	1.87	4	-	-
Cl (mg L^{-1})	235-2780	935.31	804.205	460.5	250	<250
SO_4 (mg L^{-1})	3-7.5	5.197	1.029	5	500	-
Ca + Mg (mg L^{-1})	2.5-13	5.76	2.111	5.25	-	-
Pb (mg L^{-1})	0-2.597	0.873	0.736	0.686	0.001	≤0.05
Cr (mg L^{-1})	0-0.324	0.116	0.077	0.114	0.05	≤0.05
Cd (mg L^{-1})	0-0.162	0.054	0.037	0.052	0.003	0.01
As (µg L^{-1})	7.55-37.85	25.03	7.21	23.76	10	50
Cu (mg L^{-1})	0-0.173	0.016	0.029	0.007	2	2
Ni (mg L^{-1})	1-5	2.542	0.999	2.5	0.02	≤0.02

a As per the WHO guidelines for drinking water quality, 2nd edition. Geneva, World Health organization. 2008.
b As per Pakistan Environmental Protection Agency (Ministry of Environment), Government of Pakistan. 2008.

Heavy Metals Analysis

Table 1 also describes the descriptive statistics analysis of heavy metals (Pb, Cr, Cd, As, Cu, Ni) concentration in groundwater samples. Lead (Pb) is a toxic substance that poses a risk to human health. It is important, as in 2016, it was reported that 54,000 deaths occurred only due to Pb poisoning [22]. A particularly high dose of Pb is toxic to all humans (especially young children). The Pb concentration in our samples was observed in the range of 0-2.597 mg L^{-1} with a mean value of 0.873 mg L^{-1}, which is significantly higher than WHO (0.001 mg L^{-1}) and Pak–EPA (0.05 mg L^{-1}) limits. The reason for the high Pb level in the study area could be from corrosion of Pb-based plumbing, paints, dyes, and iron/steel mills.

Chromium (Cr) is considered an important nutrient for its insulin action effect which is attributed to its possible role in the metabolism of lipids, carbohydrates, and protein. Higher exposure to Cr leads to severe effects on the kidney, spleen, and bone marrow. In addition, higher exposure to the Cr (VI) dose was reported as having carcinogenic effects. It was noted that the Cr concentration in our analyzed samples was in the range of 0-0.324 mg L^{-1} with a mean value of 0.116 mg L^{-1}. This mean value was well above the acceptable limit of WHO and Pak–EPA (0.05 mg L^{-1}), which could be due to huge industrial activities [23, 24].

Cadmium (Cd) is present naturally in the earth's crust at a low level, but anthropogenic activities (refining, smelting, and burning fossil fuels) are responsible for Cd increases beyond acceptable limits. The Cd contents in our samples were also higher than the permissible limit (0.054 mg L^{-1}) as compared to WHO (0.003 mg L^{-1}) and Pak–EPA (0.01 mg L^{-1}) permissible limits.

Arsenic (As) is class (I) carcinogenic [25] in nature and widely distributed in the earth's crust in the form of arsenic sulfide, arsenide, and arsenate. About 150 million people are directly exposed to As poisoning (>10 µg L^{-1}) [26]. Our data indicate that the maximum As concentration was found to be 37.85 µg L^{-1} and the minimum was 7.55 µg L^{-1}. The average As concentration of 62 samples was 25.03 µg L^{-1}, which was significantly higher than the WHO limit (10 µg L^{-1}) but within the acceptable limit of Pak–EPA (50 µg L^{-1}).

Copper (Cu) is another essential micro-nutrient with an average intake of 1-4 mg day^{-1}. The human body contains about 100 mg of Cu, but higher doses of Cu create certain problems, such as cardiovascular diseases and cognitive decline. However, our results show that the mean value was 0.016 mg L^{-1}, which is well below the permissible limit of WHO and Pak–EPA (2 mg L^{-1}).

Nickel (Ni) concentration in groundwater is influenced by multiple factors such as sampling depth, pH level, and soil type. The Ni concentration obtained in this study was significantly higher (2.54 mg L^{-1}) than the permissible limits (0.02 mg L^{-1}). This could be due to Ni waste coming from chemical and industrial plants.

Multivariate Analysis

Pearson Correlation Analysis

A correlation matrix of groundwater quality parameters and heavy metals in collected samples was performed to understand the relationships between these key parameters. The critical value (r-value) for quality parameters and heavy metals in collected analyzed samples was 0.22. Therefore, any value ≥0.22 was considered to be significant at a p-value ≤0.05 (Table 2).

In case of quality parameters (TSS, Ca+Mg, CO_3, HCO_3, pH, TDS, EC, SO_4, Cl), TSS is positively correlated with Ca+Mg (r = 0.346) and HCO_3 (r = 0.451). Positive correlations of Ca+Mg with TCS (r = 0.346), HCO_3 (r = 0.465), TDS (r = 0.276), EC (r = 0.294), and SO_4 (r = 0.266), whereas negatively correlated with CO_3 (-0.33) in groundwater samples were observed. The CO_3 is negatively correlated to Ca+Mg (r = -0.334) and TDS (r = -0.265). The HCO_3, EC, TDS, SO_4, and Cl are also positively correlated (r ≥ 0.22) with each other. On the other hand, heavy metals such as As are negatively correlated to Pb (r = -0.287) and positively correlated to Cr (r = 0.394) (Table 2). A negative correlation of As with Pb is possibly due to different sources of this element, as Pb primarily comes from anthropogenic activities. Chromium is positively correlated with As, as its main origin is geogenic [21]. Therefore, the accumulation and release of these heavy metals vary for their origin in the environment. This positive correlation is attributed to common pollution sources in the study area, e.g., cement factories, thermal power plants, and the leaching of coal fly ash via soil into the drinking water table [21].

Principle Component Analysis

The principle component analysis (PCA) is a multivariate analysis tool that has been applied for the investigation of multiple hydrogeochemical parameters, i.e., water groups, redox states, and factors affecting quality parameters [26]. Groundwater samples were subjected to PCA to understand if there was any relationship between heavy metals and other groundwater quality parameters (Fig. 2) (Table 3).

Four major principle components (PC–1, PC–2, PC–3, and PC–4) affect the water quality in our collected sample results, showing 85% variance of the original data structure. Bold values in Table 3 indicate that these values correspond to each variable that may be attributed to the control hydro geochemistry of the selected area. In PC–1, TDS, EC, SO_4, Cr, pH, and As were major contributors, which could be due to high dissolved ions in the groundwater. The TSS, Ca+Mg, HCO_3, pH, and Ni were the major contributors in PC–2. These ions are ascribed to the dissolution of CO_3 minerals that might significantly influence the composition of groundwater in the study area. In PC–3 CO_3, As, Pb, and pH, are the major contributors, whereas Cu, Cd, and Cl are the major contributors in PC–4, which might be due to common pollution sources (anthropogenic activities) in the study area as disused above, e.g., cement factories and thermal power table plants [21].

The cluster analysis (CA) data is very much related to PCA analysis. The CA results assisted in explaining the groundwater quality data and suggesting patterns of related parameters. In the groundwater of the study area, two groups of parameters were reported. The dendrogram demonstrated that there are two major clusters of elements with almost equal size (Fig. 3).

In CA, similar parameters lie in the same group, while dissimilar classes lie in another group. The first cluster includes Ca+Mg, HCO_3, SO_4, pH, TSS, CO_3, Pb, and Ni, as displayed in Fig. 3, indicating that all the above-mentioned parameters originate from similar sources, such as natural and mainly industrial activities. The second cluster includes As, Cr, Cd, Cu, and Cl^-, TDS, EC, and SO_4 (Fig. 3). It is possible that the source of these group parameters may originate from parent rock materials as well as urban and industrial activities in the study area. Elevated concentrations of As, pH, and HCO_3^- were caused by the interaction of groundwater in the study area with deep aquifer sediments, which were saturated with carbonate [27]. Moreover, other heavy metals such as Cr, Cd, and Cu of this group could originate from natural (parent rock material) or anthropogenic sources. Similar results were reported in previous research as well, which indicated that weathering of rocks and industrial activities in urban areas could affect the major ions to underground water chemistry [26, 28, 29].

Exposure Risk Assessment

Non-Carcinogenic

The probability of adverse carcinogenic and non-carcinogenic effects from analyzed groundwater samples is shown in Table 4, with special emphasis on adult and children's health risk assessment. It is important to mention that all analyzed samples possessed potential health concerns for the study area population.

Non-carcinogenic, chronic daily intake dose (CDI) results show the mean value of CDI (Cr) child 7.09E-03 mg kg^{-1}, CDI (Cr) adult 3.18E-03 mg kg^{-1}, CDI (Pb) child 5.34E-02 mg kg^{-1}, CDI (Pb) adult 2.39E-02 mg kg^{-1}, CDI (Cd) child 3.30E-03 mg kg^{-1}, and CDI (Cd) adult 1.48E-03 mg kg^{-1}, respectively, which were very high and posed the potential health risks to the study area population. In addition, our results suggested that children are soft targets for these heavy metals in order of Cr>Pb>Cd. Our results correspond to previous research [30, 31].

Heavy metals HQ value was >1.00 both for adults and children. If HQ≥1.00, heavy metals (Cr and Cd) concentration in groundwater samples may be ascribed to potential non-carcinogenic risk. Our results show

Table 2. Correlation matrix of heavy metals and other groundwater quality parameters in sampled of Lahore Pakistan.

Variables	TSS	Ca+Mg	CO_3	HCO_3	Cu	As	Ni	Pb	Cr	Cd	pH	TDS	EC	SO_4	Cl
TSS	1	0.346	-0.057	0.451	0.051	0.133	0.336	0.116	-0.077	-0.115	-0.043	-0.004	0.002	0.081	0.043
Ca+Mg	0.346	1	-0.334	0.465	-0.108	-0.103	0.095	-0.132	-0.060	0.095	0.018	0.276	0.294	0.266	-0.008
CO_3	-0.057	-0.334	1	-0.109	0.037	-0.269	0.070	0.268	-0.193	-0.065	0.067	-0.265	-0.216	-0.106	-0.062
HCO_3	0.451	0.465	-0.109	1	-0.077	-0.008	0.223	-0.067	-0.240	0.107	0.213	0.131	0.136	0.098	-0.018
Cu	0.051	-0.108	0.037	-0.077	1	-0.057	-0.031	-0.142	0.006	-0.006	-0.101	0.010	0.030	0.068	0.298
As	0.133	-0.103	-0.269	-0.008	-0.057	1	-0.165	-0.287	0.394	0.011	0.077	-0.038	-0.078	-0.058	0.153
Ni	0.336	0.095	0.070	0.223	-0.031	-0.165	1	0.068	-0.079	-0.036	-0.024	-0.335	-0.313	-0.189	-0.245
Pb	0.116	-0.132	0.268	-0.067	-0.142	-0.287	0.068	1	-0.179	-0.140	0.285	-0.137	-0.085	0.158	-0.166
Cr	-0.077	-0.060	-0.193	-0.240	0.006	0.394	-0.079	-0.179	1	0.144	-0.049	0.325	0.334	0.348	0.359
Cd	-0.115	0.095	-0.065	0.107	-0.006	0.011	-0.036	-0.140	0.144	1	0.101	0.205	0.181	0.038	-0.143
pH	-0.043	0.018	0.067	0.213	-0.101	0.077	-0.024	0.285	-0.049	0.101	1	0.208	0.219	0.215	-0.056
TDS	-0.004	0.276	-0.265	0.131	0.010	-0.038	-0.335	-0.137	0.325	0.205	0.208	1	0.982	0.788	0.300
EC	0.002	0.294	-0.216	0.136	0.030	-0.078	-0.313	-0.085	0.334	0.181	0.219	0.982	1	0.847	0.353
SO_4	0.081	0.266	-0.106	0.098	0.068	-0.058	-0.189	0.158	0.348	0.038	0.215	0.788	0.847	1	0.392
Cl	0.043	-0.008	-0.062	-0.018	0.298	0.153	-0.245	-0.166	0.359	-0.143	-0.056	0.300	0.353	0.392	1

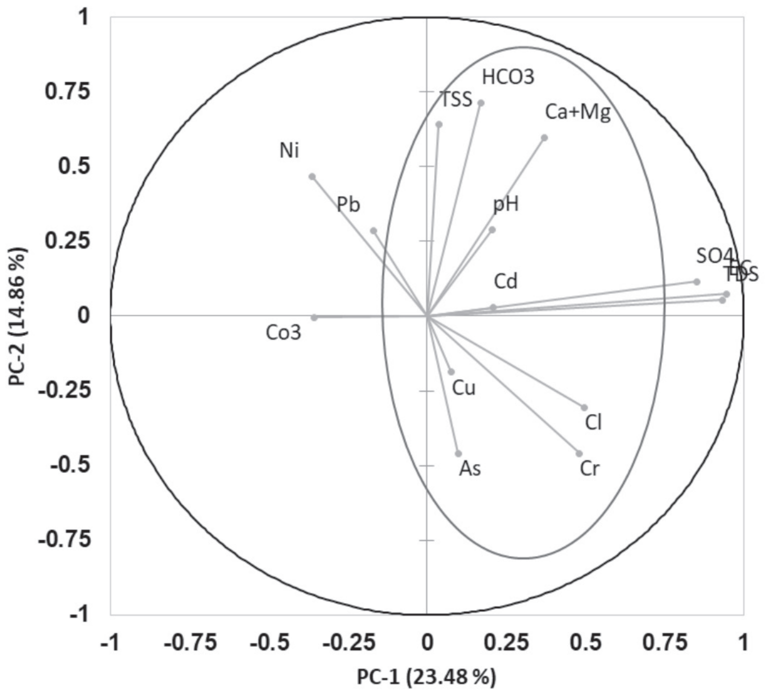

Fig. 2. The PCA of groundwater quality parameters in Lahore, Pakistan.

Table 3. Principal component analysis of heavy metals and various other water quality attributes for groundwater samples collected from Lahore, Pakistan.

	PC-1	PC-2	PC-3	PC-4	PC-5
TSS	0.001	0.409	0.069	0.188	0.041
Ca+Mg	0.137	0.356	0.148	0.004	0.006
CO_3	0.128	0.000	0.329	0.043	0.011
HCO_3	0.029	0.510	0.095	0.001	0.000
Cu	0.006	0.035	0.001	0.373	0.245
As	0.010	0.211	0.252	0.032	0.195
Ni	0.131	0.217	0.042	0.023	0.027
Pb	0.029	0.082	0.456	0.002	0.147
Cr	0.232	0.210	0.035	0.000	0.143
Cd	0.043	0.001	0.008	0.288	0.206
pH	0.042	0.083	0.203	0.101	0.040
TDS	0.869	0.003	0.018	0.009	0.011
EC	0.895	0.005	0.034	0.001	0.007
SO_4	0.725	0.013	0.085	0.022	0.016
Cl	0.246	0.093	0.003	0.324	0.009

that the mean value of HQ (Cr) child is 2.36, HQ (Cr) adult is 1.06, HQ (Cd) child is 6.61, and HQ (Cd) adult is 2.96, respectively. Moreover, the HQ indices of Cr and Cd metals were comparable in groundwater reported by [32] and in drinking water by [33].

Carcinogenic Risk

The carcinogenic risk (CR) index was estimated for Cr both for children and adults. Our results indicate a higher degree of CR value of Cr for the study area population. We found the mean value for Cr–child

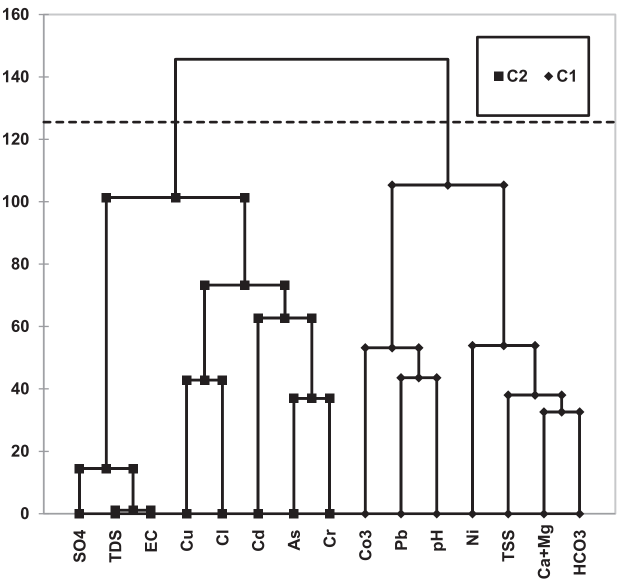

Fig. 3. Cluster Analysis of groundwater quality parameters in Lahore, Pakistan.

3.55E-03 and Cr–adult 1.59E-03 in the study area. Moreover, the CR values exceeded the permissible level of US-EPA (10^{-6} to 10^{-4}) more in children than adults (Table 4). This high concentration level is attributed to rapid industrialization, dramatic climate change, and other economic activities.

Previous studies also suggested that the carcinogenic risk from oral exposure to heavy metals is the most dominant phenomenon [34]. In addition, this pathway was probably regarded as the main pathway for heavy metal exposure. Hence, serious consideration should be employed in CR phenomena for the local population who are directly exposed to these elements through drinking water.

Conclusion

In this study, we assessed the concentration of physico-chemical parameters and heavy metals in groundwater samples (n = 62) of Lahore, Pakistan. We found that the concentration of physico-chemical parameters (TDS, Cl) and heavy metals (Pb, Cr, Cd, As) exceeded WHO permissible limits in groundwater. Multivalent analyses (person correlation matrix and PCA) were performed to understand the relationship between quality and heavy metal parameters. In this study, we found comparable levels of Ca+Mg, Cl, SO_4, CO_3, HCO, pH, and heavy metals in the groundwater of the study area (Lahore, Pakistan). Owing to high concentrations of Cr, Pb, and Cd, high cancer and non-carcinogenic risks were reported in the study area. As compared to adults, children were more prone to health problems, possibly due to their lower body weight. The non-carcinogenic risk was maximum for Cd in children, while the carcinogenic risk was found to be higher for Cr in children in the study area. This study highlights the importance of human health regarding health risks associated with groundwater quality parameters and possible exposure to heavy metals present in groundwater used for drinking purposes. In short, water quality parameters, heavy metal analysis with multivariant analysis, and exposure risk assessment were performed, and found that prolonged exposure to a higher concentration of heavy metals in water may lead to serious health hazards to the residents. Therefore, future research should be done on the mineralogical composition of underground sediments to understand the origin of these heavy metals and to understand the hydrogeochemistry of the study area.

Table 4. Summary of potential health risks caused by drinking groundwater containing high concentration of heavy metals, to children and adults in Lahore, Pakistan.

Parameters	Min	Max	Mean	SD	Median
CDI (Cr) Child (mg kg^{-1})	1.83E-04	1.98E-02	7.09E-03	4.71E-03	6.97E-03
CDI (Cr) Adult (mg kg^{-1})	8.22E-05	8.88E-03	3.18E-03	2.11E-03	3.12E-03
CDI (Pb) Child (mg kg^{-1})	6.12E-05	1.59E-01	5.34E-02	4.50E-02	4.20E-02
CDI (Pb) Adult (mg kg^{-1})	2.74E-05	7.12E-02	2.39E-02	2.02E-02	1.88E-02
CDI (Cd) Child (mg kg^{-1})	1.22E-04	9.91E-03	3.30E-03	2.26E-03	3.18E-03
CDI (Cd) Adult (mg kg^{-1})	5.48E-05	4.44E-04	1.48E-03	1.01E-03	1.42E-03
HQ (Cr) Child	0.06	6.61	2.36	1.57	2.32
HQ (Cr) Adult	0.03	2.96	1.06	0.70	1.04
HQ (Cd) Child	0.24	19.82	6.61	4.53	6.36
HQ (Cd) Adult	0.11	0.89	2.96	2.03	2.85
Cancer Risk (Cr, Child)	9.17E-05	9.91E-03	3.55E-03	2.35E-03	3.49E-03
Cancer Risk (Cr, Adult)	4.11E-05	4.44E-03	1.59E-03	1.05E-03	1.56E-03

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Conflict of Interest

The authors declare no conflict of interest.

References

1. XU H., YANG X., WANG D., HU Y., CHENG Z., SHI Y., ZHENG P., SHI L. Multivariate and spatio-temporal groundwater pollution risk assessment: A new long-time serial groundwater environmental impact assessment system. Environmental Pollution, **317**, 120621, **2023**.
2. YANG X., DU J., JIA C., YANG T., SHAO S. Groundwater pollution risk, health effects and sustainable management of halocarbons in typical industrial parks. Environmental Research, **250**, 118422, **2024**.
3. ADNAN M., XIAO B., ALI M.U., XIAO P., ZHAO P., WANG H., BIBI S. Heavy metals pollution from smelting activities: A threat to soil and groundwater. Ecotoxicology and Environmental Safety, **274**, 116189, **2024**.
4. ADEYEMI A.A., OJEKUNLE Z.O. Concentrations and health risk assessment of industrial heavy metals pollution in groundwater in Ogun state, Nigeria. Scientific African, **11**, e00666, **2021**.
5. SUN L., LIU T., DUAN L., TONG X., ZHANG W., CUI H., WANG Z., ZHENG G. Spatial and temporal distribution characteristics and risk assessment of heavy metals in groundwater of Pingshuo mining area. Environmental Geochemistry and Health, **46** (4), 141, **2024**.
6. DOGRA N., SHARMA M., SHARMA A., KESHAVARZI A., MINAKSHI, BHARDWAJ R., THUKRAL A.K., KUMAR V. Pollution assessment and spatial distribution of roadside agricultural soils: a case study from India. International Journal of Environmental Health Research, **30** (2), 146, **2020**.
7. LI Y., YE Z., YU Y., LI Y., JIANG J., WANG L., WANG G., ZHANG H., LI N., XIE X., CHENG X., LIU K., LIU M. A combined method for human health risk area identification of heavy metals in urban environments. Journal of Hazardous Materials, **449,** 131067, **2023**.
8. BANGOTRA P., JAKHU R., PRASAD M., ASWAL R.S., ASHISH A., MUSHTAQ Z., MEHRA R. Investigation of heavy metal contamination and associated health risks in groundwater sources of southwestern Punjab, India. Environmental Monitoring and Assessment, **195** (3), 367, **2023**.
9. LIU D., SHI Q., LIU C., SUN Q., ZENG X. Effects of Endocrine-Disrupting Heavy Metals on Human Health. Toxics, **11** (4), 322, **2023**.
10. SALL M.L., DIAW A.K.D., GNINGUE-SALL D., EFREMOVA AARON S., AARON J.-J. Toxic heavy metals: impact on the environment and human health, and treatment with conducting organic polymers, a review. Environmental Science and Pollution Research, **27**, 29927, **2020**.
11. KAHLOWN M.A., TAHIR M.A., RASHEED H., BHATTI K.P. Water quality status, national water quality monitoring programme. Fourth Technical Report PCRWR, 5, **2006**.
12. LI Y., MI W., JI L., HE Q., YANG P., XIE S., BI Y. Urbanization and agriculture intensification jointly enlarge the spatial inequality of river water quality. Science of The Total Environment, **878**, 162559, **2023**.
13. APHA Standard Methods of Water and Wastewater, 21st ed.; American Public Health Association, Washington, DC., 2, **2005**.
14. USEPA Risk Assessment Guidance for Superfund Volume 1 Human Health Evaluation Manual (Part A) Interim Final EPA/540/l -89/002, vol. I. United States Environmental Protection Agency, Washington, D.C. **1989**.
15. REITEMEIER R. Semimicroanalysis of saline soil solutions. Industrial & Engineering Chemistry Analytical Edition, **15** (6), 393, **1943**.
16. RICE E.W., BRIDGEWATER L., ASSOCIATION A.P.H. Standard methods for the examination of water and wastewater. American public health association Washington, DC, **2012**.
17. INAM E., INOH G.G., OFFIONG N., ETIM B.B. Physicochemical characteristics and health risk assessment of drinking water sources in Okoroette Community, Eastern Coast of Nigeria. American Journal of Water Resources, **5** (1), 13, **2017**.
18. BORTEY-SAM N., NAKAYAMA S.M., IKENAKA Y., AKOTO O., BAIDOO E., MIZUKAWA H., ISHIZUKA M. Health risk assessment of heavy metals and metalloid in drinking water from communities near gold mines in Tarkwa, Ghana. Environmental Monitoring and Assessment, **187,** 1, **2015**.
19. USEPA Risk Based Screening Table-Generic, Summary Table. United States Environmental Protection Agency. Available online: http://www.epa.gov/risk/risk-based-screening-tablegeneric-tables (accessed on 31 January 2016).
20. SWRCB Domestic water quality and monitoring regulations. In: SWRCB (Ed.), California Code of Regulation Title 22 Division 4. Environmental Health. State Water Resources Control Board, California, **2006**.
21. SHARMA S., NAGPAL A.K., KAUR I. Appraisal of heavy metal contents in groundwater and associated health hazards posed to human population of Ropar wetland, Punjab, India and its environs. Chemosphere, **227**, 179, **2019**.
22. DEBNATH B., SINGH W., MANNA K. Sources and toxicological effects of lead on human health. Indian Journal of Medical Specialties, **10** (2), 66, **2019**.
23. ALSUBIH M., EL MORABET R., KHAN R.A., KHAN N.A., UL HAQ KHAN M., AHMED S., QADIR A., CHANGANI F. Occurrence and health risk assessment of arsenic and heavy metals in groundwater of three industrial areas in Delhi, India. Environmental Science and Pollution Research International, **28** (44), 63017, **2021**.
24. IDREES N., TABASSUM B., ABD ALLAH E.F., HASHEM A., SARAH R., HASHIM M. Groundwater contamination with cadmium concentrations in some West U.P. Regions, India. Saudi Journal of Biological Sciences, **25** (7), 1365, **2018**.
25. IARC International Agency for Research on Cancer Monographs on the Evaluation of Carcinogenic Risks to Humans. Arsenic, Metals, Fibres and Dusts. **2012**.

26. NATASHA BIBI I., SHAHID M., NIAZI N.K., YOUNAS F., NAQVI S.R., SHAHEEN S.M., IMRAN M., WANG H., HUSSAINI K.M., ZHANG H., RINKLEBE J. Hydrogeochemical and health risk evaluation of arsenic in shallow and deep aquifers along the different floodplains of Punjab, Pakistan. Journal of Hazardous Materials, **402** 124074, **2021**.
27. AHMED K.M., BHATTACHARYA P., HASAN M.A., AKHTER S.H., ALAM S.M., BHUYIAN M.H., IMAM M.B., KHAN A.A., SRACEK O. Arsenic enrichment in groundwater of the alluvial aquifers in Bangladesh: an overview. Applied Geochemistry, **19** (2), 181, **2004**.
28. SHAKOOR M.B., BIBI I., NIAZI N.K., SHAHID M., NAWAZ M.F., FAROOQI A., NAIDU R., RAHMAN M.M., MURTAZA G., LÜTTGE A. The evaluation of arsenic contamination potential, speciation and hydrogeochemical behaviour in aquifers of Punjab, Pakistan. Chemosphere, **199**, 737, **2018**.
29. RASOOL A., XIAO T., FAROOQI A., SHAFEEQUE M., MASOOD S., ALI S., FAHAD S., NASIM W. Arsenic and heavy metal contaminations in the tube well water of Punjab, Pakistan and risk assessment: A case study. Ecological engineering, **95**, 90, **2016**.
30. LU Y., KHAN H., ZAKIR S., IHSANULLAH KHAN S., KHAN A.A., WEI L., WANG T. Health risks associated with heavy metals in the drinking water of Swat, northern Pakistan. Journal of Environmental Science (China), **25** (10), 2003, **2013**.
31. AHMED J., WONG L.P., CHUA Y.P., CHANNA N., MEMON U.U., GARN J.V., YASMIN A., VANDERSLICE J.A. Heavy metals drinking water contamination and health risk assessment among primary school children of Pakistan. Journal of Environmental Science and Health, Part A. Toxic Hazardous Substances Environmental Engineering, **56** (6), 667, **2021**.
32. MUHAMMAD S., SHAH M.T., KHAN S. Health risk assessment of heavy metals and their source apportionment in drinking water of Kohistan region, northern Pakistan. Microchemical Journal, **98** (2), 334, **2011**.
33. KAVCAR P., SOFUOGLU A., SOFUOGLU S.C. A health risk assessment for exposure to trace metals via drinking water ingestion pathway. International Journal of Hygiene and Environmental Health, **212** (2), 216, **2009**.
34. SHAFIUDDIN AHMED A.S., HOSSAIN M.B., BABU S.M.O.F., RAHMAN M.M., SARKER M.S.I. Human health risk assessment of heavy metals in water from the subtropical river, Gomti, Bangladesh. Environmental Nanotechnology, Monitoring & Management, **15**, 100416, **2021**.