Geoscience Frontiers 12 (2021) 101128

Contents lists available at ScienceDirect

Geoscience Frontiers

journal homepage: www.elsevier.com/locate/gsf

Potentially harmful metals, and health risk evaluation in groundwater of Mardan, Pakistan: Application of geostatistical approach and geographic information system

Abdur Rashid [a],*, Muhammad Ayub [b], Asif Javed [c], Sardar Khan [d], Xubo Gao [a], Chengcheng Li [a], Zahid Ullah [a], Tariq Sardar [e], Juma Muhammad [f], Shahla Nazneen [d]

[a] School of Environmental Studies, China University of Geosciences, Wuhan 430074, PR China
[b] Department of Botany Hazara University 21300, Pakistan
[c] Department of Earth and Environmental Sciences, Bahria University Islamabad, 44000, Pakistan
[d] Department of Environmental Sciences, University of Peshawar, Peshawar 25120, Pakistan
[e] Department of Environmental Sciences, Kohat University of Science and Technology, Pakistan
[f] Department of Environmental Sciences, Shaheed Benazir Bhutto University Sherngal, Pakistan

ARTICLE INFO

Article history:
Received 17 June 2020
Received in revised form 17 November 2020
Accepted 16 December 2020
Available online 28 December 2020

Handling Editor: E. Shaji

Keywords:
Groundwater
Potential harmful metals
Health risk indices
Cluster analysis
Mineral phases

ABSTRACT

This study investigates the values of pH, total dissolved solids (TDS), elevation, oxidative reduction potential (ORP), temperature, and depth, while the concentrations of Br, and potentially harmful metals (PHMs) such as Cr, Ni, Cd, Mn, Cu, Pb, Co, Zn, and Fe in the groundwater samples. Moreover, geographic information system (GIS), XLSTAT, and IBM SPSS Statistics 20 software were used for spatial distribution modeling, principal component analysis (PCA), cluster analysis (CA), and Quantile-Quantile (Q-Q) plotting to determine groundwater pollution sources, similarity index, and normal distribution reference line for the selected parameters. The mean values of pH, TDS, elevation, ORP, temperature, depth, and Br were 7.2, 322 mg/L, 364 m, 188 mV, 29.6 °C, 70 m, 0.20 mg/L, and PHMs like Cr, Ni, Cd, Mn, Cu, Pb, Co, Zn, and Fe were 0.38, 0.26, 0.08, 0.27, 0.36, 0.22, 0.04, 0.43 and 0.86 mg/L, respectively. PHMs including Cr (89%), Cd (43%), Mn (23%), Pb (79%), Co (20%), and Fe (91%) exceeded the guideline values set by the world health organization (WHO). The significant R^2 values of PCA for selected parameters were also determined (0.62, 0.67, 0.78, 0.73, 0.60, 0.87, −0.50, 0.69, 0.70, 0.74, −0.50, 0.70, 0.67, 0.79, 0.59, and −0.55, respectively). PCA revealed three geochemical processes such as geogenic, anthropogenic, and reducing conditions. The mineral phases of $Cd(OH)_2$, $Fe(OH)_3$, FeOOH, Mn_3O_4, Fe_2O_3, MnOOH, $Pb(OH)_2$, $Mn(OH)_2$, MnO_2, and $Zn(OH)_2$ (−3.7, 3.75, 9.7, −5.8, 8.9, −3.6, 2.2, −4.6, −7.7, −0.9, and 0.003, respectively) showed super-saturation and under-saturation conditions. Health risk assessment (HRA) values for PHMs were also calculated and the values of hazard quotient (HQ), and hazard indices (HI) for the entire study area were increased in the following order: Cd>Ni>Cu>Pb>Mn>Zn>Cr. Relatively higher HQ and HI values of Ni, Cd, Pb, and Cu were greater than one showing unsuitability of groundwater for domestic, agriculture, and drinking purposes. The long-term ingestion of groundwater could also cause severe health concerns such as kidney, brain dysfunction, liver, stomach problems, and even cancer.

© 2020 Elsevier B.V. This is an open access article under the CC BY-NC-ND license (http://creativecommons.org/licenses/by-nc-nd/4.0/).

1. Introduction

Potentially harmful metal(loid)s (PHMs) are the elements having a density greater than 4000 kg/m^3, and 5 times heavier than the density of groundwater ((Lin et al., 2014); Birami et al., 2020). Most of the PHMs contain chromium (Cr), arsenic (As), nickel (Ni), cadmium (Cd), manganese (Mn), lead (Pb), zinc (Zn), cobalt (Co), copper (Cu), mercury (Hg), and iron (Fe) (da Silva et al., 2000; Rashid et al., 2019a). These PHMs act as the geogenic components and also constitute the ground floor of the earth's crust. Some of the PHMs are acting as micronutrients (Zn, Fe, Cu, and Mn) and an important part of human nutrition. The higher concentrations of most of the PHMs are toxic for human consumption (Cundy et al., 2008; Kalyoncu et al., 2012). Thus groundwater of the earth's crust is mostly used for drinking, cooking, bathing, agriculture, and other domestic needs (Rashid et al., 2019b).

In the last twenty to thirty year's industrialization, urbanization, population density, consumption of natural resources, and mining actions have been increased. As a result of these activities, the quality of groundwater in the world is deteriorating. Thus, the availability of clean drinking water resources has been reduced both in terms of quality and quantity worldwide (Javed et al., 2017; Ponsadailakshmi et al.,

---

* Corresponding author.
E-mail address: abdur.rashid@bs.qau.edu.pk (A. Rashid).

https://doi.org/10.1016/j.gsf.2020.12.009
1674-9871/© 2020 Elsevier B.V. This is an open access article under the CC BY-NC-ND license (http://creativecommons.org/licenses/by-nc-nd/4.0/).

2018; Rashid et al., 2019b). The presence of the PHMs in groundwater is harmful for human beings even at a trace amount (da Silva et al., 2000; Rashid et al., 2019b). These groundwater ingredients mostly occur as a result of geologic sources. Thus, groundwater contamination has occurred worldwide due to geochemical, biological, and anthropogenic sources. Therefore, the evaluation and human health risk assessment are of prime importance (Liu and Ma, 2020). Additionally, the geochemical modeling through the representation of geographic information system (GIS) has received great attention in the recent decade (Babiker et al., 2005; Chappells et al., 2014; Jones et al., 2014; Singh et al., 2014; Khan et al., 2015; Rashid et al., 2019a; Egbueri, 2020; Islam et al., 2020; Khalid and Shahid, 2020).

Globally, numerous research studies have been reported drinking groundwater contamination with PHMs. The available literature reported PHM contamination in different countries of the world such as China (Li et al., 2014; Xu et al., 2015), Bangladesh (Bodrud-Doza et al., 2020), India (Bhutiani et al., 2016; Ravindra and Mor, 2019; Aithani et al., 2020), Saudi Arabia (Mohamed and Al Shehri, 2009; Zumlot et al., 2013; Ghrefat et al., 2014), and Australia (Saha et al., 2017). About PHMs contamination the scientific community of Pakistan conducted research studies in Charsadda, Buner, and Lower Dir (Khan et al., 2013b; Javed et al., 2017; Rashid et al., 2019b), Peshawar Basin (Shah and Tariq, 2006), Chitral and Flood plain of River Swat (Rashid et al., 2018; Rashid et al., 2019c), Lower Dir, and sub-district Dargai (Rashid et al., 2019a; Rashid et al., 2020). Thus, it is noted that the drinking groundwater of many areas in Pakistan is contaminated with PHMs, due to natural and anthropogenic inputs that prevail in the surrounding water aquifers.

Both natural and anthropogenic processes contribute to PHMs pollution in groundwater sources (Shah et al., 2012; Rashid et al., 2019a). The geogenic sources include weathering of rocks, minerals dissolution, oxidation-reduction, sediment deposition, and geothermal water (Macklin and Klimek, 1992; Buchet and Lison, 2000; Maity et al., 2020). Though several anthropogenic actions, such as wastewater effluents, acid mine drainage, petrochemicals, landfill, mining activities, agriculture practices, vehicular emissions, and surface runoff increases the release of PHMs in the groundwater system as the result of the aforementioned processes. The dissolution of PHMs in the water can lead to health risks and affect the lifestyle of a human being (Ritter et al., 2002; Hussain et al., 2014; Abiriga et al., 2020; Ashraf et al., 2020).

Moreover, PHMs such as Fe, Cu, Cr, and Zn are required in specific amounts and their deficiency results in an impairment of biological processes and dysfunctions, of biological tissues. Moreover, the higher concentrations of these groundwater contaminants may cause toxicity, and human health risk (Shah et al., 2012; Soltani et al., 2015; Rashid et al., 2019a). Therefore, the ingestion of polluted groundwater may result in several waterborne diseases (Rashid et al., 2019a). Thus, the concentration of PHMs in drinking water sources shows great variability. The moderate to low concentration may result in hearing loss, learning disabilities, inhibit growth, flu, and gastrointestinal diseases. Whereas, excessive exposure to PHMs can lead to the following symptoms including sleep disorder, vomiting, irritability, constipation, fatigue, cramps, and poor appetite. However, the higher concentration of Pb in children can cause neurological damage, coma, convulsions, organ failure, and ultimately death. Additionally, Pb accumulates and stores within the body structure such as bones, brain, and kidney (Singh et al., 2018).

Moreover, several mathematical and geostatistical techniques are used to assess, monitor, and predict variability of groundwater dynamics and geochemical profile (McKnight and Finkel, 2013; Jones et al., 2014). Though evaluating and calculating the water quality is an additional multidimensional action since groundwater depends on various hydrogeochemical variables (Bodrud-Doza et al., 2016; Rashid et al., 2019a). Many researchers have developed a wide range of statistical methods for the estimation of water quality (Islam et al., 2017; Murasingh et al., 2018). Most of the recent studies showed that the application of GIS, geostatistical and statistical approaches are helpful to assess and understand the mechanism of source apportionment and PHM contamination in groundwater bodies (McKnight and Finkel, 2013; Rani and Chaudhary, 2015; Gunarathna et al., 2016). However, geostatistical methods are considered to be more reliable and appropriate for predicting and forecasting spatial data. This approach is unique and considered as a cumulative of geostatistical and spatial methods (Nas, 2009; Oke et al., 2013). Similarly, it is a far substantial tool to collect spatial autocorrelation between groundwater sampling points (Bhuiyan et al., 2016). Nevertheless, Kriging, nearest neighbour estimate, Inverse Distance Weighted (IDW), and Spline are the four reliable methods for spatial interpolation approaches. All these approaches are generally applied to explain and interpolate the spatial variability of water contaminants (Gunarathna et al., 2016). Among these methods, the most widely used method is the ordinary kriging (Webster and Oliver, 2007). Maps of groundwater parameters are used to categorize the locations contaminated with PHMs (Gorai and Kumar, 2013). The groundwater PHMs such as Cr, Ni, Cd, Co, Zn and Fe within the contiguous location of the study area have been calculated. Therefore, ordinary kriging and log normal kriging have been used to generate spatial distribution maps of PHMs in the groundwater. Thus ordinary kriging maps known as OK maps are calculated through ArcGIS approach (Magesh et al., 2013).

Besides, spatial interpolation multivariate statistical techniques were employed to strengthen the scope of this study. The multivariate statistic includes factor analysis (FA), principal component analysis (PCA), cluster analysis (CA), and correlation coefficient (r). These statistical tools help to find out the contamination sources and identifying the cluster within the groundwater samples of the study area. The ingestion of contaminated groundwater sources can lead to a health risk index (HRI). The assessment of the hazard index (HI) of groundwater of District Lower Dir could explain the severity of groundwater ingestion (Rashid et al., 2019b). Unfortunately, the drinking groundwater of the world is extremely contaminated with PHMs that were recognized as a result of natural as well as anthropogenic actions such as smelting and industrialization. Heavily contaminated groundwater with PHMs frequently leads to higher HRI due to chronic daily intake (CDI). Naturally, the toxicity levels of PHMs mostly depend on the ingestion and consumption rate of water (Muhammad et al., 2011; Belkhiri et al., 2017; Rashid et al., 2019a, 2019b; Saleh et al., 2019; Jehan et al., 2020).

In the Northern-Pakistan, the anthropogenic actions viz. (unplanned urbanization, industrialization, mining actions, agricultural practice, and domestic wastes) and natural processes including leaching, weathering, percolation, and minerals dissolution have led to the deterioration of groundwater quality (Azizullah et al., 2011). In the present study, the geochemical profiles, saturation indices, and health risks of the industrial zone and control area are compared. Based on the above considerations, the major aims of this study to: (i) investigate the concentration profiles of PHMs such as Cr, Ni, Cd, Mn, Cu, Pb, Co, Zn, and Fe in groundwater of Mardan; (ii) to assess the health risk index and measured the persistency, genotoxicity and carcinogenic behaviors of PHMs via oral ingestion of groundwater; (iii) to identify the mineral phases of the studied parameters through PHREEQC interactive software 3.4.0-12927; and (iv) to understand the spatial distribution modeling of PHMs and source provenance by multivariate statistical tools and ArcMap GIS 10.3.

2. Material and methods

2.1. Description of the study area

The study area presents in district Mardan within the geographic coordinate between 34°05′N–34°32′N and 71°48′E—72°25′E (Fig. 1), with a total area of 1630 km^2. The study area can be broadly divided into three zones based on the environmental set up that includes the urbanized/industrialized zone (Shergarh and Takht Bhai) and the non-industrialized zone (control area called Surkhabi). Later on, these

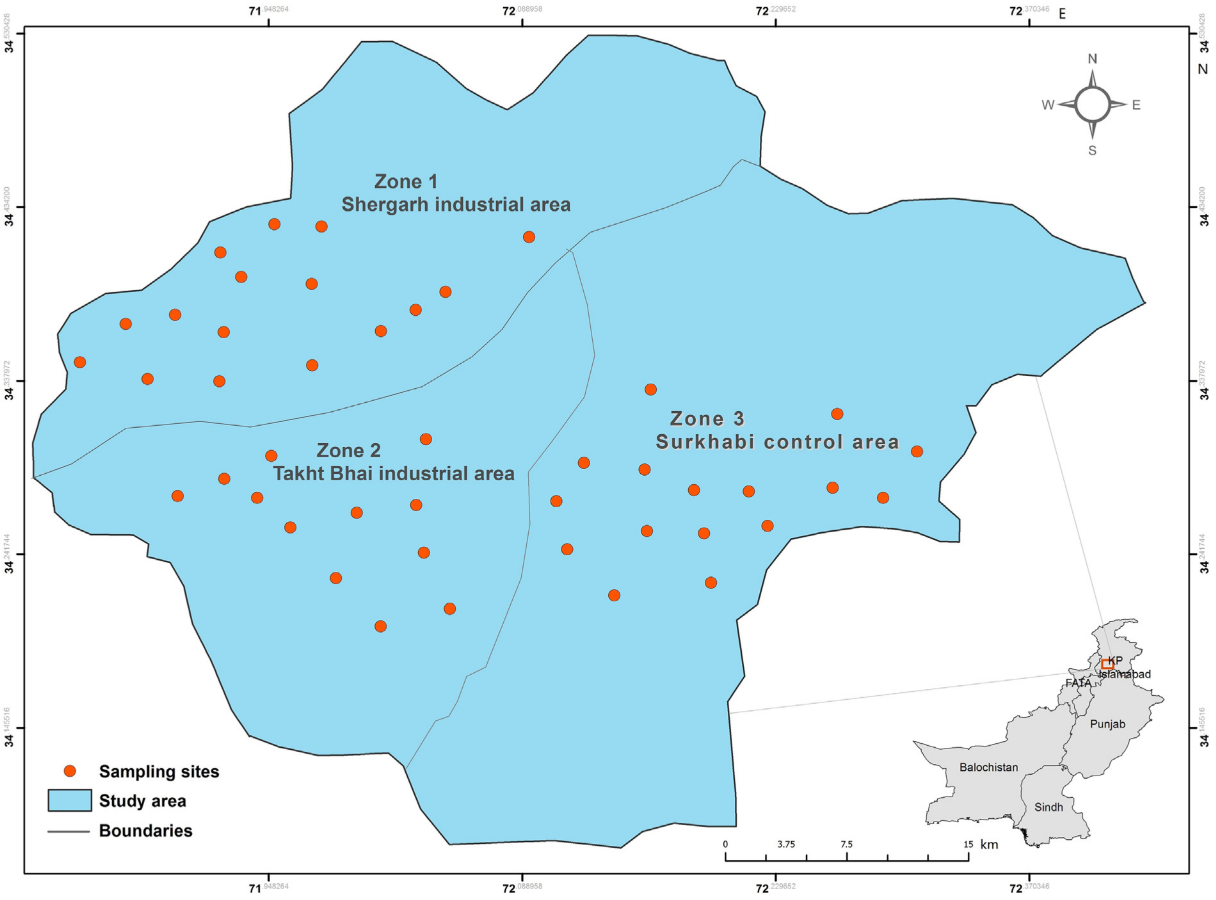

Fig. 1. Map showing the locations of groundwater samples collected from study area.

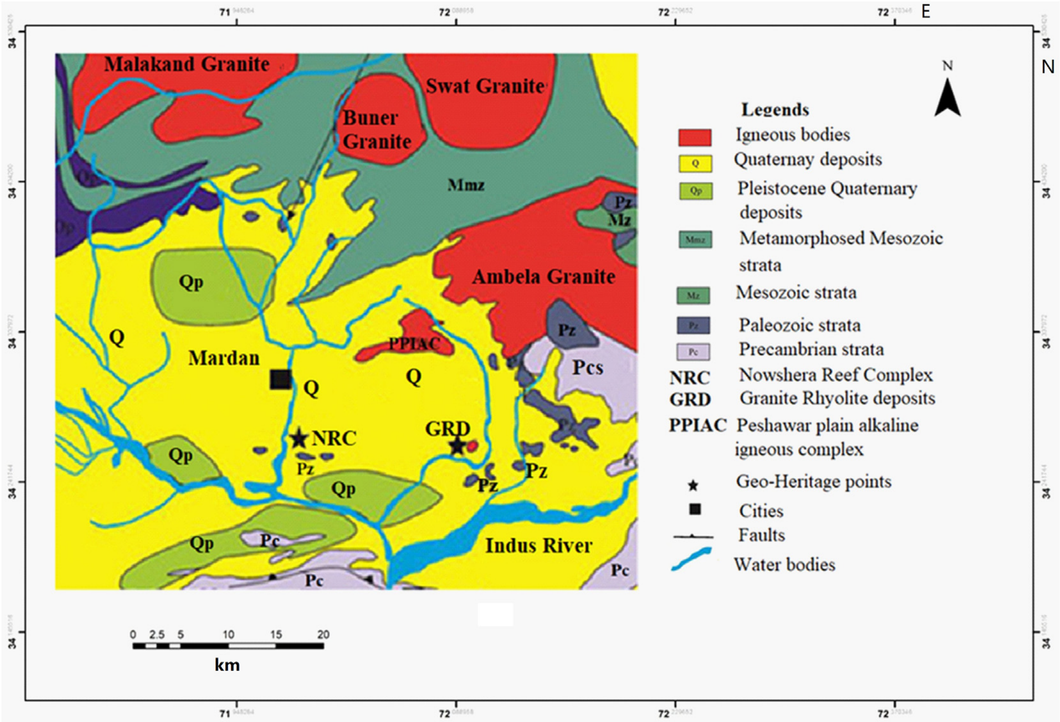

Fig. 2. Geological map reveals the geological formations within the study area.

areas are called Zone 1, Zone 2, and Zone 3, respectively. The urbanized/industrial zone includes several brick kilns car washing stations etc., while the non-industrial zone contains no industrial units as well as other anthropogenic activities. The groundwater samples in the study area were mostly collected from the human household settings. The percentage area covered in Zone 1, Zone 2, and Zone 3 were 70%, 68%, and 65%, respectively. Moreover, the study area is divided into two parts, the southwestern part is considered a plain area and the northern side contains small hills. Plain areas consist of fertile land, where the people of the area do farm by growing vegetables and other crops to earn money and fulfill their basic needs of life including food, water, health care, sanitation, clothing, shelter, and education.

2.2. Hydrology and hydrogeology

Hydrology of the area reveals the quantity and amount of drinking water utilized by common people. Mostly, groundwater sources like dug well, hand pump, bore well, tube well water was used by the people for domestic purposes. The groundwater is mostly derived from shallow and the deeper aquifer present in the study area. The primary recharge source of most of the water well is mostly precipitation, while the 2nd recharge source is the Dargai irrigation canal that is extracted from River Swat at Batkhela head station whose water flowing towards district Mardan.

The hydrogeology of the area is composed of igneous and metamorphosed rocks (see Fig. 2), that contain minerals of PHMs. The potential minerals contain in igneous rocks are potassium feldspar, plagioclase, feldspar, quartz, muscovite, biotite, mica, pyroxenes, hornblende, amphiboles, and olivine. Whereas, metamorphic rock deposits contain feldspar, mica, quartz, calcite, hornblende, epidote, garnet, chlorite, kyanite, staurolite, and sillimanite. However, rhyolite is an igneous granitic rock having an aphanitic crystalline structure. While Precambrian rock is known as the prime geologic age, composed of various sedimentary, and magmatic rocks that contain gold, copper, chromite, nickel, and iron deposits. Moreover, granite is found in igneous terrain occurs as an assemblage of rock that contains minerals viz. mica, quartz, feldspar, and hornblende. Though granite contains 20%–60% quartz, and 35% alkali feldspar minerals, and the rest of the proportion contains PHMs.

The Quaternary deposits contain unconsolidated sediments such as a stream, channel, moraine, gravels, beach sand, glacial drift, and floodplain deposits. Moreover, the Quaternary deposits contain minerals like calcite, paragonite, kaolinite, muscovite, and dolomite. Additionally, the study area contains Mesozoic rock composed of coal-bearing strata and mudstone. Mesozoic rock mostly occurs in the lower to middle Jurassic period whose thickness ranged from 100 m to 700 m. Whereas, the size of lower cretaceous rocks ranges of 50–350 m respectively. Moreover, Mesozoic rock provides the basis for the Cenozoic era which occurs between 230 and 65 million years ago. While Mesozoic age consists of three geologic periods namely, Triassic, Jurassic, and Cretaceous. The Paleozoic period is known as the Phanerozoic eon which represents ancient life. The geological composition contains fossil which is distributed throughout the globe that contains a sedimentary rock. Paleozoic rocks of the study area include different minerals viz. fluorite, celestine, and marcasite, dolostone, and limestone. Whereas, the deposits of sphalerite and galena minerals contain Zn and Pb sulfides in the study area (Ahmed, 1984; Gul et al., 2015). The weathering and dissolution of these rocky minerals play a vital role in the contamination of the groundwater system present in the area.

2.3. Groundwater sampling and instrumentation

Drinking groundwater samples (n=44) were collected in May 2018, from three selected zones (Zone 1, Zone 2, and Zone 3) of Mardan such as Shergarh (groundwater n=15), Takht Bahi (groundwater n=13), and Surkhabi (groundwater n=16). The percentage area covered in Zone 1, Zone 2, and Zone 3 were 70%, 68%, and 65% respectively. The collected groundwater samples were investigated for basic water parameters and PHMs to notice the influence of geogenic and anthropogenic inputs and spatial variability on the drinking water quality of the study area. All groundwater samples were collected from different sources such as tube well, hand pump, bore-well, storage tank, and dug well. Groundwater samples were collected by adopting a random sampling strategy. Approximately, each sample was collected after a 600–1000 m distance. Most of the samples were taken from highly populated areas within the urbanized/industrialized and control areas of Mardan, Pakistan. Each sample was collected after flowing of water for five minutes' time interval. The sampling points and elevation were recorded by a global positioning system (GPS, eTrex Garmin). Basic water parameters like pH, temperature, oxidative reduction potential (ORP), and total dissolved solids (TDS) of groundwater samples were measured in situ. The values of pH were measured with the Orion Model 420A. Whereas, temperature and TDS were determined by Orion 5 Star conductivity meter (manufacturing country, USA). The ORP was determined by HM digital ORP-200 manufactured country Scotland. The samples collected for chemical analysis were acidified with 3% HNO_3 (purity 65%; Merck company). Moreover, all groundwater samples were filtered via 0.45 μm filter paper, for the security measure of the sophisticated instrument such as Inductively Coupled Plasma Mass Spectrometry (ICP-MS). The concentrations of PHMs such as Cr, Ni, Cd, Mn, Cu, Pb, Co, Zn, and Fe were measured by ICPMS (Agilent 7500 ICP-MS), the manufacturing country United States of America (USA). Groundwater samples were cautiously handled to evade the introduction or loss of PHMs during the preparation of the sample and its analysis. The chemical reagents and materials were of analytical grade and kept in Teflon and free-metal containers.

2.4. Face to face interview

Questioner survey was conducted with the help of an environmental scientist and medical experts. The medical expert team contains two research scientists and two medical doctors. The research team includes experts from the University of Peshawar (UOP) and Mardan Medical Complex (MMC) for this study. The head of the expert' team asked several questions like age, gender, ingestion of groundwater sources, profession, finance, education, and health status of the individuals of the area. After the interview session, it was concluded that that most of the people belong to low financial status, and cannot pay for mineral water. Therefore, most of the residents used groundwater for domestic needs. Moreover, most of the resident was uneducated and does not care about their health status. Furthermore, most local people used up water from hand pumps, springs, tube well, dug well, and bore well to complement their needs. In rural areas of Pakistan, women act as household managers and are responsible for fetching wood and drinking water from surrounding areas. So most time females are busy with water collection from the surrounding sources. Thus, females were mostly exposed to a health hazard in the study area.

2.5. Health risk assessment

Health risk assessment was performed to record the toxicity level of PHMs in groundwater. There are three pathways through which human beings were exposed such as oral ingestion, dermal, and inhalation. Oral ingestion still considers the most exposing route among the three. PHMs exposure via oral ingestion has been calculated in this study based on chronic daily intake ($CDI_{Ingestion}$), Hazard Quotient ($HQ_{Ingestion}$), and Hazard Index ($HI_{Ingestion}$) formulas. These formulas help to calculate and assess the exposure level and ingestion rate (IR) of PHMs through the consumption of groundwater. Human health risk assessment (HHRA) was calculated according to US EPA designed equations (Singh et al., 2018).

$$\mathrm{CDI}_{\mathrm{Ingestion}} = \frac{\mathrm{CPHMs} \times \mathrm{IR} \times \mathrm{EF} \times \mathrm{ED}}{\mathrm{BW} \times \mathrm{AT}} \tag{1}$$

$$\mathrm{HQ}_{\mathrm{Ingestion}} = \frac{\mathrm{CDI}_{\mathrm{Ingestion}}}{\mathrm{RfD}_{\mathrm{Ingestion}}} \tag{2}$$

$$\mathrm{HI} = \sum \mathrm{HQ}_{\mathbf{Ingestion}} \tag{3}$$

whereas, C_{PHMs} = potential harmful metals concentration (mg/L), IR = ingestion rate (2 L/day for adult and 1 L/day for children), EF = exposure frequency (365 days/year), ED = exposure duration (350 days), BW = body weight (72 kg for adult, and 32 kg for children), AT = averaging time (72 × 365 days). To calculate the health risk assessment all the values of groundwater variables were obtained from the USEPA database, except $C_{\mathrm{PHMs},}$ and RfD (Epa, 1991; EPA, 2002). The value of RfD was obtained from (Salud et al., 1997). Moreover, the Hazard Index (HI) values for groundwater contaminants were recorded by summing the HQ values of each PHMs. The HI indices results after calculation less than one (<1) is declared as no risk while higher than one (>1) is pose a greater risk for the entire human population (Avigliano and Schenone, 2015; Singh et al., 2018).

2.6. Multivariate statistical analysis

Descriptive statistics, such as range, mean and standard deviation (SD) and correlation coefficient matrix (r) values, were calculated after quantification of data. The SD reflects the degree of dispersion to distribute different parameters sources, but indirectly designate the action of a particular parameter in the investigated system (Han et al., 2006). Statistical analysis was commonly used to recognize multiple parameters to understand the related phenomenon. Multivariate statistics including PCA, CA were calculated using the XLSTAT version 2014, SPSS Statistical package version 20, and Microsoft Excel 2013. The PCA was used to find out the contamination sources, and their percentage contribution of contaminant. Whereas, CA was used to understand the similarity and dissimilarity index. PCA results mostly accompanied by the eigenvalues greater than one and factor loading contribute 70% cumulative was considered significant. Whereas, cluster analysis determined the groundwater data in the form of distinguishing cluster, which clearly describes the cluster comparison. Thus, the lowest, moderate, polluted, and severely polluted clusters were obtained. These methods defined the relationship between studied PHMs, and physicochemical variables for better interpretation of groundwater data.

2.7. Groundwater mineral phase and GIS mapping

Groundwater mineral phases were constructed using PHREEQC interactive software 3.4.0-12927. The mineral phases of Cd, Fe, Mn, Pb, and Zn were calculated accordingly. Whereas, ArcMap GIS-10.3 software designed by ESRI were specifically used to develop study area and spatial interpolation geostatistical maps of Mardan Basin. Groundwater numerical data were integrated into ArcGIS to develop spatial interpolation maps, based on the Kriging method. With the help of these models, groundwater contamination with PHMs were visualized and used to calculate the missing information regarding groundwater contamination in the study area.

2.8. Quality control (QC) and quality assurance (QA)

To attain accuracy and preciseness in the result of analytical data, routine quality control checks, standards operating protocols, reagent blanks, standard calibration, and triplicate analyses were employed according to (Lloyd and Heathcote, 1985). The chemicals used during analysis were purchased from Germany (Merck Company). All glassware were thoroughly washed with deionized water and a 30% HCl solution to remove the contamination. After washing, glassware was oven-dried. Reagent blanks were used after six samples to monitor and investigate the contamination, the concentration of blank was subtracted from the groundwater concentration. PHMs were analyzed with the help of ICPMS (Agilent 7500 ICP-MS) as mentioned earlier.

3. Results and discussion

3.1. Geochemistry of groundwater

Table 1 summarizes the geochemistry of groundwater collected from three populated areas of Mardan Basin, Pakistan. The pH values in Shergarh, Takht Bahi, and Surkhabi areas were found in the range of 6.5–7.5, 6.6–7.6, and 6.7–8.0, respectively. Similarly, in Shergarh, Takht Bahi, and Surkhabi areas, the TDS range was observed as 245–370, 280–360, and 280–450 mg/L, respectively. Likely, the elevation from sea level in the selected three regions were 290–380, 310–390, and 340–480 m, respectively. The ranges of ORP and temperature in groundwater samples of Shergarh, Takht Bahi, and Surkhabi were reported as 145–210 mV, 160–215 mV, and 165–260 mV, and 28.6–31 °C, 26.5–28.7 °C and 28.6–30.9 °C, respectively. Whereas, the depth for the three regions were also greatly varied (25–70, 35–80, and

Table 1
Geochemical profile of groundwater samples (n=44) collected from three zones of study area.

Locations	Shergarh (n=15)		Takht Bahi (n=12)		Surkhabi (n=16)		
Statistic	Range	Mean ± SD	Range	Mean ± SD	Range	Mean ± SD	WHO guidelines
pH	6.5–7.5	7.1±0.3	6.6–7.6	7.1±0.3	6.7–8.0	7.3± 0.4	6.5–9.2
TDS (mg/L)	245–370	306±36	280–360	313±26	280–450	344± 59	400
Elevation (m)	290–380	335±27	310–390	344±28	340–480	413±48	–
ORP (mV)	150–210	172±18	160–215	184±18	165–260	206± 32	–
Temp (°C)	28.6–31	30.3±0.63	26.5–28.7	27.9±0.67	28.6–30.9	30.2± 0.59	–
Depth (m)	25–70	49±13	35–80	58±13	55–125	101±18	–
Br (mg/L)	0.12–0.32	0.21±0.05	0.13–0.35	0.22±0.07	0.10–0.25	0.18±0.04	
Cr (mg/L)	0.04–0.53	0.30±0.16	0.05–0.23	0.10±0.07	0.21–1.17	0.67± 0.30	0.05
Ni (mg/L)	0.03–0.50	0.21±0.11	0.01–0.55	0.22±0.20	0.05–0.79	0.35± 0.19	3.0
Cd (mg/L)	0.01–0.06	0.03±0.02	0.01–0.06	0.04±0.02	0.03–0.23	0.15± 0.06	0.05
Mn (mg/L)	0.01–0.67	0.21±0.19	0.11–0.65	0.32±0.21	0.01–1.09	0.32± 0.24	0.5
Cu (mg/L)	0.02–0.45	0.10±0.08	0.02–1.23	0.38±0.46	0.02–0.98	0.59± 0.30	2.0
Pb (mg/L)	0.01–0.45	0.13±0.11	0.01–0.13	0.05±0.05	0.10–0.90	0.43± 0.12	0.01
Co (mg/L)	0.04–0.15	0.05±0.03	0.02–0.15	0.05±0.04	0.01–0.05	0.03± 0.01	0.04
Zn (mg/L)	0.01–0.75	0.21±0.15	0.02–1.23	0.50±0.49	0.04–1.69	0.58± 0.42	3
Fe (mg/L)	0.28–2.30	0.83±0.53	0.28–1.35	0.84±0.34	0.05–1.38	0.89± 0.40	0.3

55–125 m, respectively) in the study area. The Br contents in the groundwater samples were observed in the range of 0.12–0.32, 0.13–0.35, and 0.10–0.25 mg/L, respectively.

Likewise, the contents of Cr, Ni, and Cd in groundwater samples of Shergarh, Takht Bahi, and Surkhabi were also varied (0.04–0.53, 0.05–0.23 and 0.21–1.17 mg/L; 0.03–0.50, 0.01–0.55 and 0.05–0.79 mg/L; and 0.01–0.06, 0.01–0.06, and 0.03–0.23 mg/L, respectively). Likely, the contents of Mn, Cu, and Pb in groundwater samples of Shergarh, Takht Bahi, and Surkhabi were also varied (0.01–0.67, 0.11–0.65 and 0.01–1.09 mg/L; 0.02–0.45, 0.02–1.23 and 0.02–0.98 mg/L; and 0.01–0.45, 0.01–0.13, and 0.15–0.90 mg/L, respectively). Similarly, the contents of Co, Zn, and Fe in the aforementioned three areas were also varied (0.04–0.15, 0.02–0.15 and 0.01–0.05 mg/L; 0.01–0.75, 0.02–1.23 and 0.04–1.69 mg/L; and 0.28–2.30, 0.28–1.35 and 0.05–1.38 mg/L, respectively), in the study area.

The minimum pH was reported in the Shergarh (Zone 1), whereas the highest pH was observed in the Surkhabi area (Zone 3). The lowest and highest TDS contents were reported in Shergarh and Surkhabi areas, respectively. Moreover, the highest dissolution of PHM contents occurred in groundwater aquifers with slightly acidic to alkaline pH and higher electrical conductivity (EC) in most regions of the study area. The TDS contents of all groundwater samples showed satisfactory results and thus found within the recommended guidelines set by the World Health Organization (WHO). The overall temperature of the groundwater sources ranged between 26.5and –31.0 °C. It is an indirect indicator of water pollution. Additionally, higher temperature delivers an appropriate environment for contagious microbial growth. The highest and lowest ORP values were reported in the groundwater samples of the Surkhabi and Shergarh areas. Whereas, the highest and lowest temperature was recorded in Shergarh and Takht Bahi areas. While temperature and ORP considered being the indirect variables that greatly influenced the geochemistry of groundwater

The highest and lowest Cr were reported in Surkhabi and Shergarh areas. The highest Cr concentration in groundwater of the study area may be attributed to the urban sewage system, dumping of solid waste, domestic and leather effluents (Khan et al., 2011). Whereas, the lowest and highest values of Ni were found in Takht Bahi and Surkhabi areas. Most of the findings of this study consistent with those reported by (Majidano and Khuhawar, 2009), in the drinking water of Nawabshah, Sindh (Pakistan). The concentration of Ni was compared with the WHO guideline value of 3.0 mg/L, which revealed that all groundwater samples were within the safe limit (WHO, 2011). The prime geogenic source of Ni contamination in the groundwater system is attributed to leaching from mafic and ultramafic rock (Muhammad et al., 2011; Shah et al., 2014; Rashid et al., 2019a). Whereas, its artificial sources include steel alloy, electroplating, ghee, fabrication, automobiles, batteries, electronic components, jewelry, sinks, utensils, surgical clips, coins, and kitchen appliances. The highest Cd was recorded in Surkhabi and Lowest in Shergarh and Takht Bahi areas. The highest contamination of Mn and Cu was recorded in Takht Bahi, whereas the lowest was reported in Shergarh and Surkhabi areas. The highest contamination of Pb was observed in Surkhabi and the lowest was recorded in Shergarh and Takht Bahi areas. The lowest content of Co was recorded in Surkhabi and highest in the Shergarh area. The average value of Co in the present study was found higher than those recorded by (Shah et al., 2012). Co is still reported as an important nutrient and vital component of vitamin B12. Usually, Co has lower toxicity, but, concentration around 1 mg/kg may cause health risk (DeZuane, 1997). Similarly, the highest and lowest content of Zn in groundwater samples was observed in Shergarh and Surkhabi areas. Whereas, the highest and lowest Fe contamination were found in the Surkhabi and Shergarh zone of the study areas.

3.2. Factors affecting groundwater chemistry

3.2.1. Effect of pH

The range and mean values of pH in three areas of Mardan Basin viz. Shergarh, Takht Bhai, and Surkhabi were slightly varied (6.5–7.5 and 7.1 ±0.3, 6.6–7.6 and 7.1±0.3, and 6.7–8.0, and 7.3± 0.4, respectively). The groundwater pH results showed slight differences between these three areas. The groundwater samples were slight acidic to slightly alkaline in nature. The reducing condition of water showed higher stability and mobility of PHMs in the surrounding aquifer (Kumpiene et al., 2008). Therefore, the pH of groundwater plays an important role in the geochemistry of PHMs. Thus, different dissolved species of PHMs in an aqueous medium mostly depend on the pH. At lower to neutral pH values, PHMs usually occur in cation form with the highest ionization and greater mobility. Due to higher pH, PHMs usually react with anions and form complexes, therefore, the oxidation states are affected and speciation of PHMs occurs in groundwater (Taşar et al., 2014).

Moreover, both positive and negative species of PHMs have existed with pH values from 6.5 to 9.0. The oxidation and reduction of PHMs depend upon the oxidation and reduction potentials of the chemical reactions of contaminants under the groundwater aquifer. The different valence states of PHMs can be detected at different pH values (Sari and Tuzen, 2008). The concentration of Pb in groundwater increased at lower pH values. But, at higher pH values Pb showed immobilization, due to precipitation processes (Kumpiene et al., 2008). Moreover, pH is considered the most significant parameter that affects the behavior of PHMs and causes the reduction of PHMs from the groundwater matrix. Most of the published research papers reported that lower pH (<4) hinders the adsorption of PHMs. Whereas, the most effective pH values have been observed between 5 and 7. In light of the above discussion, the pH of the groundwater aquifer should be maintained neutral and their level ranged between 6.5 and 9.0.

3.2.2. Effect of temperature

The temperature of the groundwater system is considered another most important parameter for the evaluation of PHMs. The range and mean values of temperature in the three areas (Shergarh, Takht Bahi, and Surkhabi) were observed as 28.6–31 °C and 30.3 °C±0.63 °C, 26.5–28.7 °C and 27.9 °C±0.67 °C, 28.6–30.9 °C and 30.2 °C± 0.59 °C, respectively. The highest temperature was recorded in the industrial area, whereas the lowest temperature was reported in the control area. The temperature of the water medium depends upon the pH and ORP levels of groundwater. Moreover, PHMs contents of groundwater decreased as a result of higher temperatures due to the tendency of ions to remain in the aqueous form (Sari and Tuzen, 2008).

3.2.3. Oxidation-reduction potential

The range and mean values of ORP in the three areas like Shergarh, Takht Bahi, and Surkhabi were 150–210 mV and 172±18 mV, 160–215 mV and 184±18 mV, 165–260 mV and 206± 32 mV respectively. The lowest ORP was observed in the groundwater of the Shergarh area, while the highest ORP was found in the Surhkhabi control area. A similar trend was observed for the highest content of ORP. Thus, the industrial areas show minimal ORP as compared to the control area. Thus, the groundwater of the control area is more oxidizing in nature. Therefore, pH and ORP showed a positive significant coefficient value ($r=$ 0.72) (Table S1). Oxidation-reduction potential (ORP) is an important parameter of a chemical reaction. During a redox reaction, one component of a reaction loses electrons, and other components gain an electron to establish redox potential. The groundwater containing an excess of the oxidizing agent has a positive ORP value. Whereas, reducing agents potentially has a negative ORP value. Most of the groundwater ORP results are positive which reflects the oxidizing condition of groundwater in the surrounding aquifer.

3.3. Human health risk exposure assessment

A human health risk exposure survey was conducted for the estimation of risk exposure in the study area. This questioner survey includes two environmental research scientists of the University of Peshawar (UOP) and two Medical doctors of Mardan Medical Complex (MMC). The medical team visited different groups of individuals such as children age (1–16 years), and adults (17–55 years) in the study area. The majority of people cumulative 70% of the local respondents claimed that the industrial set p and commercial activities of the study area are responsible for the contamination of the groundwater and health status of the study area. The common diseases reported by the expert team found in the local community were listed below. The common diseases were included irritability, constipation, sleep disorder, hearing loss, fatigue, cramps, gastrointestinal disease, neurological damage, learning disabilities, poor appetite, inhibit growth, organ failure, flu, vomiting, coma, and convulsions.

To understand the exact environmental guidelines and increased health distresses for the local community, and the consequences of PHMs in groundwater were assessed in terms of chronic daily intake (CDI), Hazard Quotient (HQ), and Hazard Index (HI). In this study, CDI, HQ, and HI via oral ingestion route for two groups of population viz. children and adults based on the USEPA standards have been calculated and their results were found in Table 2. Thus, most people in the study area were greatly exposed to PHMs due to groundwater intake. To capture the current status of the residents of the three areas viz. Shergargh, Takht Bahi, and Surkhabi of Mardan Basin, health risk assessment (HRA) for children and adults were measured.

The average CDI values of Cr, Ni, Cd, Mn, Pb, Cu, and Zn in children were 0.02, 0.04, 0.003, 0.04, 0.03, 0.05, and 0.07, respectively. Similarly, the CDI values of Cr, Ni, Cd, Mn, Pb, Cu, and Zn for adults were observed to be 0.04, 0.04, 0.002,0.04, 0.03, 0.05, and 0.06 respectively. Likely, the average HQ values of Cr, Ni, Cd, Mn, Pb, Cu, and Zn for children of Marden Basin were 0.03, 2.05, 4.48, 0.31, 0.89, 1.52, and 0.24 respectively. Likewise, the average HQ values of Cr, Ni, Cd, Mn, Pb, Cu, and Zn in adults of the study area were recorded to be 0.03, 1.75, 3.48, 0.27, 0.76, 1.30, and 0.20 respectively.

Thus, this study reveals that the HQ values of Ni, Cd, Pb, and Cu for both children and adults were greater than one. Therefore, the groundwater water ingestion of the three areas was considered vulnerable regarding their health risk prospects. The health indices (HI) values of this study for Cr, Ni, Cd, Mn, Pb, Cu, and Zn were observed to be 0.10, 5.28, 5.59, 0.80, 2.29, 3.92, and 0.60, respectively. Therefore, the higher values above one, in this study were reported for Ni, Cd, Pb, and Cu. Therefore, these elements are considered vulnerable to human health and cause various health implications. The HI values of Cd were found higher due to their low RfD values. The results of this study were compared with the study conducted by (Khan et al., 2013a) and (Rashid et al., 2019a). Thus, the comparison showed that the findings of this study were similar to the above-mentioned research work.

3.4. Correlation between potential toxic metals

Mostly, PHMs in groundwater have a complex relationship among them. It was noticed that different processes controlling the relative abundance of PHMs in groundwater. Table S1 represented the Pearson correlation coefficient matrix (r) values of PHMs in groundwater sources of the Mardan Basin. Mostly the correlation matrix (r) values supported the groundwater results of PCA. Table S1 values in bold are different from zero and are significant at the level alpha 0.05. The values above 0.50 were considered significant that frequently influenced the relationship of groundwater variables. Positive values represent that the water variable was significantly influenced by different processes. Whereas negative values do not affect the saturation of water chemistry. Therefore, Person correlation coefficient (r) significant pair at 0.05 alpha level with 95% confidence calculated to be; pH vs. ORP (r= 0.50), pH vs. Temperature (r=0.58), pH vs. Cr (r=0.47), pH vs. Cu (r= 0.50), pH vs. Zn (r=0.57), pH vs. Fe (r=0. 56), TDS vs. ORP (r=0.59), TDS vs. Cr (r= 0.48), ORP vs. Cr (r= 0.50), ORP vs. Cu (r= 0.48), Tem vs. Cr (r= 0.48), Cr vs. Ni (0.56), Cr vs. Cd (r= 0.69), Cr vs. Pb (r= 0.59), Ni vs. Cd (r= 0.45), Ni vs. Cu (r=0.55), Cd vs. Pb (r= 0.59), Cu vs. Zn (r= 0.63) respectively. The positive correlation between Cr and Ni in groundwater suggests the geogenic origin of Cr in the study area. Most of the results in this study were influenced and dependent on pH, TDS, and ORP.

3.5. The concentration of dissolved species in groundwater

Table S2 represents the dissolved species of groundwater of the three populated areas of Mardan Basin, Pakistan. The mean concentration of H^+, OH^-, Cd^{+2}, Cu^+, Cu^{2+}, Fe^{2+}, Mn^{2+}, Pb^{2+} and Zn^{2+} in Mardan Basin were observed to be 0.0001, 0.0002, 0.03, 0.001, 0.03, 0.3, 0.25, 0.08, 0.36 respectively. Similarly, the range values of aforementioned species were observed as 0.0000–0.0003, 0.0001–0.0016, 0.0300–0.2298, 0.0001–0.1488, 0.0002–0.2416, 0.0275–1.5340, 0.0100–1.0880, 0.0061–0.5313, and 0.0097–1.6160 respectively. The highest values were reported for Cd^{2+}, Cu^{2+}, Fe^{2+}, Mn^{2+}, Pb^{2+}, and Zn^{2+} respectively (Table S2). The mean and standard deviation values of above-dissolved species were reported in (Table S2). The highest mean concentration of H^+ up to 0.0001±0.0001 was found similar in all areas. Whereas, OH, Cd^{2+}, Cu^{2+}, Pb^{2+}, and Zn^{2+} concentration up to 0.0005±0.0005, 0.1508±0.0577, 0.0890±0.0846, 0.2481±0.1597, and 0.5443±0.4044 were found in Surkhabi area. While Cu^+, Fe^{2+}, Mn^{2+} up to 0.0143± 0.0424, 0.3809±0.2865, and 0.3398±0.2189 were found in Takht Bahi area. Whereas, Fe^{3+} and Mn^{3+} show 0.0000±0.0000 concentration. So, therefore, these two dissolved species have no significant importance.

Table 2

Average chronic daily intake (CDI), hazard quotient (HQ), and health indices (HI) pose through oral ingestion of contaminated groundwater consumed by local people.

	CDI Children								HQ in Children						
Locations		Cr	Ni	Cd	Mn	Pb	Cu	Zn	Cr	Ni	Cd	Mn	Pb	Cu	Zn
Shergarh	average	0.05	0.03	0.003	0.03	0.02	0.02	0.03	0.03	1.67	3.10	0.22	0.58	0.46	0.11
Takht Bahi	average	0.01	0.03	0.003	0.04	0.01	0.05	0.08	0.01	1.67	3.25	0.32	0.25	1.36	0.26
Surkhabi	average	0.10	0.06	0.004	0.06	0.07	0.10	0.10	0.07	2.82	4.10	0.40	1.84	2.76	0.33
	CDI in adults								HQ in adults						
Shergarh	average	0.04	0.03	0.002	0.03	0.02	0.01	0.03	0.03	1.43	4.10	0.19	0.50	0.39	0.10
Takht Bahi	average	0.01	0.03	0.002	0.04	0.01	0.04	0.07	0.01	1.43	4.25	0.27	0.21	1.16	0.22
Surkhabi	average	0.09	0.05	0.002	0.05	0.06	0.09	0.08	0.06	2.41	5.05	0.34	1.58	2.37	0.28
	HI								0.10	5.28	5.59	0.80	2.29	3.92	0.60
Risk exposure															

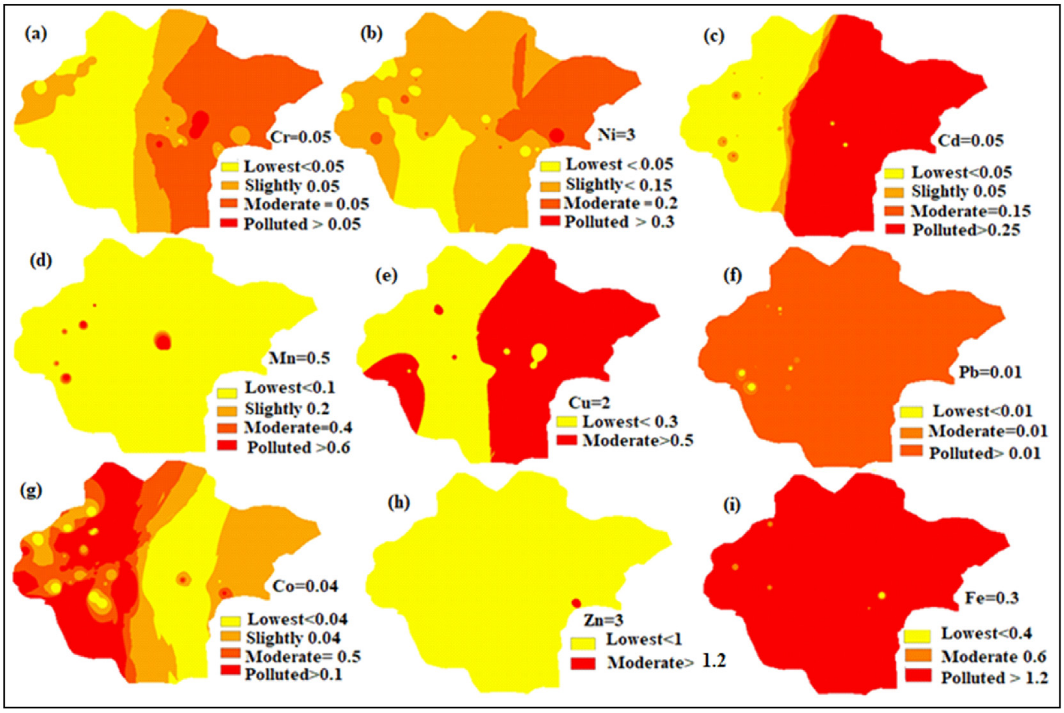

Fig. 3. Spatial distribution mapping of selected PHMs viz. (a) Cr, (b) Ni, (c) Cd, (d) Mn, (e) Cu, (f) Pb, (g) Co, (h) Zn, and (i) Fe in groundwater system of the study area.

3.6. Geospatial modeling and distribution of pollution hotspot

Geospatial analysis and modeling were calculated through GIS software version 10.3. The geospatial modeling and distribution pattern of PHMs in groundwater contamination were represented in (Fig. 3). The PHM contents were first incorporated via Ordinary Kriging protocol to design the GIS model using the interpolation technique (McKnight and Finkel, 2013;Bhuiyan et al., 2016;Javed et al., 2017). The achieved geochemical maps of PHMs such as Cr, Ni, Cd, Mn, Cu, Pb, Co, Zn, and Fe have shown mobilization in groundwater of the study area (Fig. 3). All these groundwater constituents show various degrees of contamination which were lowest, slightly, moderate, and polluted. Therefore, groundwater aquifer showed variability in concentrations of water variables. The resulting distribution maps explained groundwater contaminants (see Fig. 3).

Cr is geospatially distributed in the groundwater aquifer of the study area (Fig. 3a). The contamination of Cr in water aquifer is highly dominated. Therefore, four different classes were designed such as lowest, slightly, moderate, and polluted. All these classes were represented by yellow, brown, dark brown, and red colour. The mean concentrations obtained by these classes were 0.04, 0.05, 0.06, and 0.2 mg/L respectively. Similarly, Ni is spatially distributed in the groundwater aquifer (Fig. 3b). Likely Cr four classes were constructed for Ni. Four different classes were obtained by Ni which includes lowest, slightly, moderate and polluted. The colour obtained were yellowish, brown, dark brown, and red respectively. The spatial distribution of Ni showed satisfactory results. Thus, all the groundwater samples revealed suitability for drinking and domestic consumption. The mean concentrations of Ni for Lowest, slight, moderate, and polluted classes were recorded to be 0.05, 0.15, 0.2, and 0.3 mg/L respectively.

Similarly, Cd is spatially distributed in the water aquifer, fabricating four classes that were most probably lowest, slightly, moderately, and polluted (Fig. 3c). The lowest class was characterized by a yellow colour, slightly lower with brown, moderately polluted by dark brown, and polluted with red colour. The mean concentrations of the above classes were 0.04, 0.05, 0.15, and 0.3 mg/L, respectively. Likely, Mn is distributed in the drinking water represented the lowest, slightly, moderately, and polluted classes obtaining yellowish, brown, dark brown, and red colour (Fig. 3d). The mean concentrations of Mn in the aforementioned four classes were 0.08, 0.18, 0.4, and 0.7 mg/L respectively. Whereas, Cu is distributed in the study area and represented two classes by owing the lowest and moderately polluted (Fig. 3e). The mean concentration of Cu was 0.2, and 0.7 mg/L, respectively. However, the groundwater Cu concentration for drinking purposes is suitable. Regarding, Cu concentration all drinking water samples were found within the guidelines set by the WHO. Therefore, water should be used safely for domestic needs. Likewise, the spatial distribution sequence of Pb briefly showed (see Fig. 3f). Similarly, four classes were constructed for Pb pollution in the groundwater. The colour attained by the lowest, moderately and polluted classes were yellowish, brown, and dark brown. The concentrations of Pb were 0.01, 0.02, and 0.5 mg/L, respectively in the study area. Also, Co was spatially distributed and characterized in four different classes like lowest, slightly, moderately, and polluted owing to yellow, brown, dark brown, and red colour. The mean concentration of Co for lowest, slightly, moderately and polluted classes were 0.03, 0.04, 0.5, and 0.6 mg/L, respectively (Fig. 3g). Similarly, Zn revealed spatial distribution patterns in groundwater having two different classes such as lowest and polluted (Fig. 3h). The mean concentrations of Zn were 1.0 and 1.23 mg/L, respectively. These classes owing yellow and brown colour for their spatial distribution. Similarly, the Fe contamination in the groundwater aquifers was recorded as (Fig. 3i). The colour owing by groundwater aquifers were yellow, moderately, and polluted classes. The mean concentrations of Fe in the groundwater aquifers were 0.35, 0. 57, and 1.5 mg/L, respectively. These colours represented Lowest, moderately, and polluted classes in the study areas. Thus, the distribution pattern of PHMs shows that groundwater is contaminated with Cd, Cr, Pb, Co, Mn, and Fe. Therefore, the residents of the area are advised to take safe groundwater sources for drinking and domestic needs.

Table 3
Chemical formula of dissolved minerals and its statistical values in groundwater of Mardan Basin, Pakistan.

SI	Shergarh (n=15)		Takhtbahi (*n*=11)		Surkhabi (*n*=17)		
Statistic	Range	Mean ± SD	Range	Mean± SD	Range	Mean ± SD	Formula
Cadmium Hydroxide	−5.27 to −3.03	−4.17±0.65	−5.54 to −2.98	−4.23±0.77	−4.29 to −1.60	−2.94±0.83	$Cd(OH)_2$
Iron Hydroxide	2.60−−4.24	3.69±0.49	2.69–4.49	3.63±0.57	2.11–4.49	3.88±0.67	$Fe(OH)_3$
Goethite	8.70−−10.33	9.76±0.49	8.70–10.46	9.63±0.56	8.2–10.5	9.95±0.66	FeOOH
Hausmannite	−11.78 to −3.61	−6.96±2.57	−10.72 to −2.45	−7.07±2.85	−8.90 to 0.86	−4.07±3.38	Mn_3O_4
Hematite	5.43−−11.70	8.56±0.99	5.43–12.94	8.28±1.12	6.44–14.03	8.9±1.3	Fe_2O_3
Maganite	−5.89 to −2.83	−4.04±0.93	−5.32 to −2.17	−3.91±1.06	−4.76 to −1.16	−2.98±1.26	MnOOH
Lead Hydroxide	1.04–2.95	1.99±0.57	0.71–2.33	1.39±0.48	1.48–4.24	2.92±0.86	$Pb(OH)_2$
Pyrochroite	−6.25--4.11	−5.00±0.69	−5.78 to −3.53	−4.81±0.77	−5.51 to −2.87	−4.20±0.88	$Mn(OH)_2$
Pyrolusite	−10.52--6.47	−8.15±1.21	−10.21 to −6.34	−8.45±1.33	−9.39 to −4.33	−6.87±1.65	MnO_2
Zinc Hydroxide	−2.90–0.05	−1.42±1.04	−3.09 to 0.30	−1.28±1.12	−2.22–1.14	−0.29±1.00	$Zn(OH)_2$
ionic strength	0.0004–0.01	0.002±0.001	0.0005–0.005	0.003±0.001	0.002–0.01	0.00±0.001	
Iterations	4.00–4.00	4.00±0.001	4.00–4.00	4.00±0.00	4.00–4.00	4.00±0.00	
TH	111.01–111.02	111.01±0.001	111.01–111.02	111.01±0.002	111.01–111.02	111.01±0.002	
TO	55.51–55.51	55.51±0.001	55.51–55.51	55.51±0.002	55.51–55.51	55.51±12.1	

3.7. Mineral phases of PHMs in groundwater

Table 3 lists the statistical results of groundwater for mineral phases and their findings were found in the form of mean, and standard deviation. The results explained the saturation indices SI of minerals phases for Cd, Fe, Mn, Pb, and Zn. The mean, and SD values of Cadmium Hydroxide, Iron Hydroxide, Goethite, Hausmannite, Hematite, Maganite, Lead Hydroxide, Pyrochroite, Pyrolusite, and Zinc Hydroxide in the groundwater samples of Mardan Basin were reported to be −4.17±0.83, 3.63 ±0.57, 9.76±0.49, −4.96±2.57, 8.56±0.99, −3.91±1.06, 1.99±0.57, −5.00±0.69, −6.87±1.65, and −0.29±1.00 respectively. Similarly, the range values of the aforementioned minerals were reported (see Table 3).

The highest mean and SD concentration of Cadmium Hydroxide, Hausmannite, and Pyrolusite, were reported up to −2.94±0.83, −4.07 ±3.38, and −6.87±1.65 in Surkhabi (control area). The lowest mean and SD concentration of Cadmium Hydroxide, Hausmannite, and Pyrolusite, were observed up to −4.23±0.77, −7.07±2.85, −8.45±1.33, in Takhbahi industrial area. Whereas, the highest Iron Hydroxide, Hematite, Lead Hydroxide up to 3.88±0.67, 8.9±1.3, 2.92±0.86, in Surkhabi (control area). Similarly, the lowest concentrations of the Iron Hydroxide, Lead Hydroxide were recorded to be 3.63±0.57, and 1.39±0.48 in the Takht Bahi industrial area. While the highest concentration of Goethite, Maganite, Pyrochroite, and Zinc Hydroxide up to 9.95±0.66, −4.04±0.93, −5.00±0.69, and −1.42±1.04 I was found in the Shergarh area. Whereas, the lowest Geothite concentration up to 9.63±0.56 in Takht Bahi. The lowest Magnate, Pyrochroite, and Zinc Hydroxide concentration up to −4.04±0.93, −5.78 to −3.53, and −1.42±1.04 was observed in Shergarh industrial area.

3.8. Cluster analysis

Cluster analysis (CA) is an important application tool, used to analyze groundwater data into different clusters based on similarity and dissimilarity index. As a result, the most similar data fall within the same cluster and varying data fall in another cluster. In this study 44 groundwater samples were analyzed for similarity and dissimilarity index. According to CA analysis, three clusters were constructed viz. C1, C2, and C3 (Fig. 4a). All the groundwater variables were arranged and designed within three groups differentiated by three different colours (Fig. S1). Within the cluster, the variability is 37.35% and between the clusters, the variation is 62.65%. The distance between the class centroid for the lowest polluted cluster C1 was recorded as 0, 101.50, and 158. Likely, the distance for moderately polluted cluster C2, reported as 101.50, 0, and 124.61. Similarly, for severely polluted cluster C3 the distance is calculated to be 158, 124.61, and 0 respectively. The number of samples present in the three clusters C1, C2, and C3 represented 26, 12, and 6 groundwater samples. The maximum samples occupied cluster C1, followed by moderate, and severely polluted clusters.

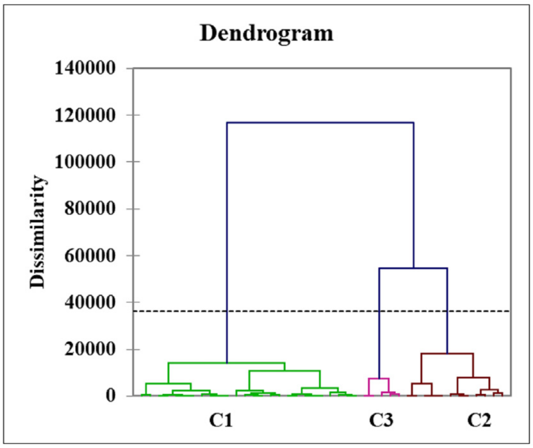

Fig. 4. Clustering analysis (CA) shows C1, C2, and C3 reveals lower, moderate, and polluted clusters.

The physicochemical variables such as pH, TDS, elevation, ORP, temperature, depth, Br, and PTMs viz. Cr, Ni, Cd, Mn, Cu, Pb, Co, Zn, and Fe values of class centroids for the lowest polluted cluster C1 were recorded as 6.8, 306, 336.15, 175, 29.4, 52, 0.22, 0.21, 0.195, 0.03, 0.23, 0.18, 0.12, 0.05, 0.28, and 0.80 respectively. Also, for moderate polluted cluster C2 the class centroid values were recorded to be 7.2, 315.83, 422.5, 192, 29.9, 101.3, 0.19, 0.59, 0.42, 0.16, 0.32, 0.63, 0.35, 0.04, 0.62, and 0.84 respectively. Likewise, for severely polluted cluster C3 the class centroid values were observed as 7.7, 424, 394, 247, 30.02, 100.8, 0.17, 0.77, 0.23, 0.11, 0.41, 0.70, 0.46, 0.02, 0.71, and 1.19 respectively.

3.9. Quantile-Quantile (Q-Q) plotting

Quantile-Quantile (Q-Q) plotting represented groundwater data of physicochemical parameters in the form of a scatter plot. It is a graphical method used to plot data of quantiles of the first data set versus the second data set. The first data set has given name expected normal value and the second data set has observed values. When a data set has plotted in the SPSS software, the expected normal and observed values arrange up and down at a 45° reference line. The values of the quantile found in a straight diagonal line represented normal distribution.

The results of Q-Q normal plotting of groundwater were represented in (Fig. S2). The normal Q-Q box plot of pH, TDS, ORP, temperature, Ni, Mn, Cr, Cu, Pb, Cd, Co, Zn, and Fe showed that the quantile of one data (expected normal values) versus second data set (observed values) showed a straight reference line at 45°. The correlation R^2 values of the aforementioned values of pH, TDS, ORP, temperature, Ni, Mn, and Cr were observed to be 0.987, 0.918, 0.929, 0.887, 0.958, 0.885, and 0.910 respectively (Fig. S2). However, Cu, Pb, Cd, Co, Zn, and Fe were observed to be 0.876, 0.856, 0.882, 0.733, 0.882, and 0.987 respectively (Fig. S2). The highest quantile and straightness of the reference line was observed for pH and Fe in the groundwater data set and their correlation coefficient R^2 values were 0.987 and 0.987 respectively.

3.10. Principal component analysis

To measure all the geochemical processes occurring in the study area principal component analysis (PCA) approach was used to understand the correlation among groundwater variables. Table S3 lists the PCA results for groundwater (n=44) for 16 variables. To reduce multivariate problems and relevancy of groundwater data, Pearson's correlation matrix and data standardization process (Z score) was applied (Koklu et al., 2010). This study revealed four rotated principal components (PC) viz. PC1, PC2, PC3, and PC4 which explain 73% variability. Whereas, overall loading factors were attributed to be sixteen (see Fig. 5a).

The first component PC1 explained 35%, PC2 explained 14.85%, PC3 explained 12.38%, and PC4 explained 8.74% of the variability with eigenvalues of 5.64, 2.38, 1.98, 1.40, respectively (Table S3). Though, PC1 and PC2 were designed in the biplot and represented 50.10% variability (Fig. 5b) because the first two components specifically described the majority of groundwater variables and its behavior that either come from geogenic or anthropogenic sources in the study area. PC1 accounted for 35.3% of the total variability which has strong positive loading for pH, TDS, elevation, ORP, depth, Cr, Ni, Cd, Cu, Pb, and Zn and their coefficient (r) values to be calculated were 0.62, 0.67, 0.78, 0.73, 0.87, 0.69, 049, 0.74, 0.70, 0.67 and 0.59 respectively. In this study, PC1 indicated the importance of geogenic input on the physicochemical variables of groundwater and suggested that pH and TDS have an important role in the saturation of water variables. All these groundwater contaminants resulted from geochemical processes affected by pH, EC, TDS, elevation, and depth. Whereas, Cr, Ni, Cu, Pb, and Zn contaminations could take its genesis from weathering and dissolution of mafic and ultramafic rocks, water-rock interaction, galena (Pb-S), chromite mineral, and ore processing (Muhammad et al., 2011; Kelepertzis et al., 2013; Khan et al., 2013a; Rashid et al., 2019a). Moreover, Cd in the groundwater system has attributed via redox transformation process and dissolution of schistose rock and sulfide minerals added additional insight to Cd enrichment in the groundwater body (Akkajit and Tongcumpou, 2010; Rashid et al., 2019a). In this study, the overall results of PC1 were influenced by both natural and anthropogenic sources.

Similarly, PC2 represented 14.85% of total variability with an eigenvalue of 2.38 (see Table S3). This component represented strong loading for temperature, Cr, Cd, Mn, and Fe with their correlation coefficient (r) values reported as 0.60, 0.50, 0.52, −0.50, and −0.55 respectively. The water results of PC2 were greatly influenced by the temperature that ultimately enhances the increase of Cr and Cd in the study area. Whereas, higher temperature of groundwater has no significant impact on Mn and Fe. The origin of Cr in this study was attributed to chromite and ophiolitic rocks with the specification of serpentine weathering products. Whereas, Cd in the area were attributed to schistose rocks present in mafic and ultramafic terrain.

Moreover, the third component PC3 indicated 12.38% of the total variability with their corresponding eigenvalues of 1.98 (see Table S3). This component showed strong loading for pH, TDS, Ni, and Br, and their corresponding correlation coefficient (r) values were reported as −0.48 and −0.50, 0.50 and 0.70, respectively. However, in this study, Ni and Br showed negated correlation with pH, and TDS values declared that acidic environment plays an important role in the discharge of Ni, and Br in the groundwater aquifer of the study area. Moreover, the association of these compounds shows that the mining actions significantly influenced the hydrogeochemical setup of the study area. However, Br in the groundwater system is naturally found and is considered one of the potential contaminants of drinking water and causes corrosion to human soft tissues and muscles in liquid form.

The Fourth component PC4 represented 8.74% of the total variability with eigenvalues of 1.40 which have strong positive loading for Co and negated values for Br and their coefficient (r) values were 0.71 and −0.50, respectively (see Table S3). In this study, Co takes its genesis from coal-burning processes, cobalt alloys, and industrial discharges (Clark, 2015). However, the negated values of Br have no significant impact on groundwater contamination.

4. Conclusion

This study represents the occurrence and enrichment of PTMs in the groundwater sources of urbanized/industrialized and control areas. PTMs such as Cr, Cd, Mn, Pb, Co, and Fe have been observed unfit for drinking and domestic purposes due to their higher concentrations, bioavailability, and persistency. Moreover, the increasing order of the groundwater parameters were observed as: TDS > ORP > depth > temperature > pH > Fe > Zn > Cr > Cu > Mn > Ni > Pb > Br > Cd > Co. The

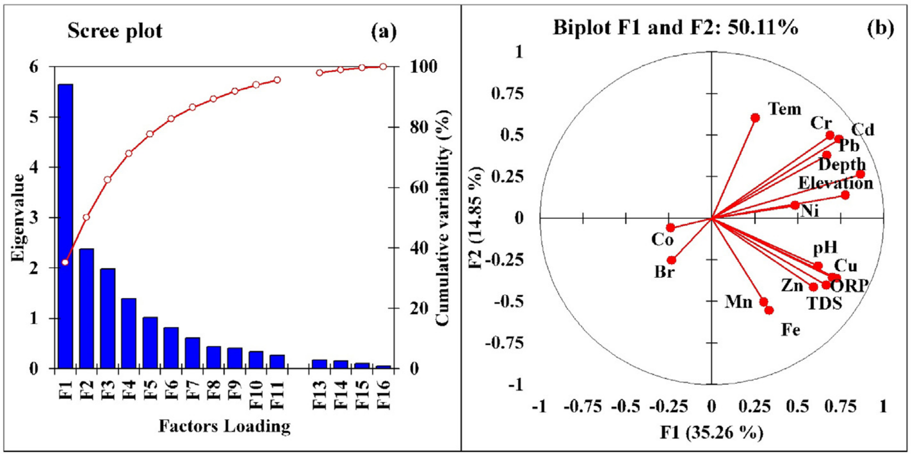

Fig. 5. (a) Overall loading factors of PCA results. (b) Contribution of the first two loading factors F1 and F2 after varimax rotation dimension.

mineral phases of $Fe(OH)_3$, FeOOH, Fe_2O_3, and $Pb(OH)_2$ showed supersaturation, while $Cd(OH)_2$, Mn_3O_4, MnOOH, $Mn(OH)_2$, MnO_2, and Zn $(OH)_2$ revealed undersaturation in the groundwater system of the study area. The result of PCA summarized three geochemical processes like natural processes viz. weathering and dissolution of mafic and ultramafic rock (Cr, Ni, Cd, and Zn), reducing condition (Mn and Fe), and anthropogenic actions viz. transportation sector, electroplating, dyes, paint, domestic waste, and ore processing for Co, and Fe. Quantile-Quantile (Q-Q) plotting techniques found the normal distribution reference line in the groundwater parameters represented a greater coefficient R^2 values above 0.77 for each parameter. Health risk exposure survey indicated that the women mostly take part in domestic activities that's why they become the household administrator. The higher HQ and HI values for Ni, Cd, Pb, and Cu represented that these groundwater sources are mostly unfit for drinking and domestic needs. The long-term exposure to PHMs may cause health-related problems. It is recommended that the groundwater sources of the study area should not be used without treatment. The local government should install a water purification plant for PHMs removal or provide alternative sources of water for drinking purposes.

Supplementary data to this article can be found online at https://doi.org/10.1016/j.gsf.2020.12.009.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

This research work has been financially supported National Natural Science Foundation of China (Grant Nos.41521001 and 41877204), the 111 Program (Grant No. State Administration of Foreign Experts Affairs & the Ministry of Education of China, B18049), and the China Postdoctoral Science Foundation (Grant No. 2018M642944).

References

Abiriga, D., Vestgarden, L.S., Klempe, H., 2020. Groundwater contamination from a municipal landfill: effect of age, landfill closure, and season on groundwater chemistry. Sci. Total Environ. 737, 140307.

Ahmed, Z., 1984. Stratigraphic and textural variations in the chromite composition of the ophiolitic Sakhakot-Qila complex, Pakistan. Econ. Geol. 79 (6), 1334–1359.

Aithani, D., Jyethi, D.S., Siddiqui, Z., Yadav, A.K., Khillare, P., 2020. Source apportionment, pollution assessment, and ecological and human health risk assessment due to trace metals contaminated groundwater along urban river floodplain. Groundw. Sustain. Dev. 11, 100445.

Akkajit, P., Tongcumpou, C., 2010. Fractionation of metals in cadmium contaminated soil: Relation and effect on bioavailable cadmium. Geoderma 156 (3–4), 126–132.

Ashraf, S., Rizvi, N.B., Rasool, A., Mahmud, T., Huang, G.G., Zulfajri, M., 2020. Evaluation of heavy metal ions in the groundwater samples from selected automobile workshop areas in northern Pakistan. Groundw. Sustain. Dev. 11, 100428.

Avigliano, E., Schenone, N.F., 2015. Human health risk assessment and environmental distribution of trace elements, glyphosate, fecal coliform and total coliform in Atlantic rainforest mountain rivers (South America). Microchem. J. 122, 149–158.

Azizullah, A., Khattak, M.N.K., Richter, P., Häder, D.-P., 2011. Water pollution in Pakistan and its impact on public health—a review. Environ. Int. 37 (2), 479–497.

Babiker, I.S., Mohamed, M.A., Hiyama, T., Kato, K., 2005. A GIS-based DRASTIC model for assessing aquifer vulnerability in Kakamigahara Heights, Gifu Prefecture, Central Japan. Sci. Total Environ. 345 (1–3), 127–140.

Belkhiri, L., Mouni, L., Narany, T.S., Tiri, A., 2017. Evaluation of potential health risk of heavy metals in groundwater using the integration of indicator kriging and multivariate statistical methods. Groundw. Sustain. Dev. 4, 12–22.

Bhuiyan, M.A.H., Bodrud-Doza, M., Islam, A.R.M.T., Rakib, M.A., Rahman, M.S., Ramanathan, A.L., 2016. Assessment of groundwater quality of Lakshimpur district of Bangladesh using water quality indices, geostatistical methods, and multivariate analysis. Environ. Earth Sci. 75 (12), 1020.

Bhutiani, R., Kulkarni, D.B., Khanna, D.R., Gautam, A., 2016. Water quality, pollution source apportionment and health risk assessment of heavy metals in groundwater of an industrial area in North India. Exposure and Health 8 (1), 3–18.

Birami, F.A., Moore, F., Faghihi, R., Keshavarzi, B., 2020. Assessment of spring water quality and associated health risks in a high-level natural radiation area, North Iran. Environ. Sci. Pollut. Res. 27 (6), 6589–6602.

Bodrud-Doza, M., Islam, A., Ahmed, F., Das, S., Saha, N., Rahman, M.S., 2016. Characterization of groundwater quality using water evaluation indices, multivariate statistics and geostatistics in Central Bangladesh. Water Science 30 (1), 19–40.

Bodrud-Doza, M., Didar-Ul Islam, S.M., Rume, T., Quraishi, S.B., Rahman, M.S., Bhuiyan, M.A.R., 2020. Groundwater quality and human health risk assessment for safe and sustainable water supply of Dhaka City dwellers in Bangladesh. Groundw. Sustain. Dev. 10, 100374.

Buchet, J.-P., Lison, D., 2000. Clues and uncertainties in the risk assessment of arsenic in drinking water. Food Chem. Toxicol. 38, S81–S85.

Chappells, H., Parker, L., Fernandez, C.V., Conrad, C., Drage, J., O'Toole, G., Campbell, N., Dummer, T.J.B., 2014. Arsenic in private drinking water wells: an assessment of jurisdictional regulations and guidelines for risk remediation in North America. J. Water Health 12 (3), 372–392.

Clark, I., 2015. Groundwater Geochemistry and Isotopes. CRC press, pp. 1–483.

Cundy, A.B., Hopkinson, L., Whitby, R.L., 2008. Use of iron-based technologies in contaminated land and groundwater remediation: A review. Sci. Total Environ. 400 (1–3), 42–51.

da Silva, E., Navarro, M., Barros, A., Mota, M., Chastinet, C., 2000. Metals in the sediments of Jauá Lake (Camaçari, Bahia, Brazil) following an episode of industrial contamination. Aquat. Ecosyst. Health Manag. 3 (4), 509–514.

DeZuane, J., 1997. Handbook of Drinking Water Quality. John Wiley & Sons, New York, pp. 1–575.

Egbueri, J.C., 2020. Heavy metals pollution source identification and probabilistic health risk assessment of shallow groundwater in Onitsha, Nigeria. Anal. Lett. 53 (10), 1620–1638.

EPA, U., 1991. Maximum contaminant level goals and national primary drinking water regulations for lead and copper; final rule. Fed. Regist. 56, 26460.

EPA, U., 2002. A Review of the Reference Dose and Reference Concentration Processes, EPA/630/P-02.

Ghrefat, H., Nazzal, Y., Batayneh, A., Zumlot, T., Zaman, H., Elawadi, E., Laboun, A., Mogren, S., Qaisy, S., 2014. Geochemical assessment of groundwater contamination with special emphasizes on fluoride, a case study from Midyan Basin, northwestern Saudi Arabia. Environ. Earth Sci. 71 (4), 1495–1505.

Gorai, A., Kumar, S., 2013. Spatial distribution analysis of groundwater quality index using GIS: A case study of Ranchi Municipal Corporation (RMC) Area. Geoinformatics and Geostatistics: An overview. Vol. 1. 2.. https://doi.org/10.4172/2327-4581.1000105.

Gul, N., Shah, M.T., Khan, S., Muhammad, S., 2015. Quantification of the Heavy Metals in the Agricultural Soils of Mardan District, Khyber Pakhtunkhwa, Pakistan. J. Global Innov. Agri. Social Sci. 2 (4), 158–162.

Gunarathna, M., Kumari, M., Nirmanee, K., 2016. Evaluation of interpolation methods for mapping pH of groundwater. International Journal of latest technology in engineering, management & applied science V, 1–5.

Han, Y., Cao, J., Posmentier, E.S., 2006. Multivariate analysis of heavy metal contamination in urban dusts of Xi'an, Central China. Sci. Total Environ. 355 (1–3), 176–186.

Hussain, M., Muhammad, S., Malik, R.N., Khan, M.U., Farooq, U., 2014. Status of heavy metal residues in fish species of Pakistan. Rev. Environ. Contam. Toxicol. 230, 111–132.

Islam, A.T., Shen, S., Bodrud-Doza, M., Rahman, M.A., Das, S., 2017. Assessment of trace elements of groundwater and their spatial distribution in Rangpur district, Bangladesh. Arab. J. Geosci. 10 (4), 95.

Islam, A.R.M.T., Siddiqua, M.T., Zahid, A., Tasnim, S.S., Rahman, M.M., 2020. Drinking appraisal of coastal groundwater in Bangladesh: an approach of multi-hazards towards water security and health safety. Chemosphere 255, 126933.

Javed, S., Ali, A., Ullah, S., 2017. Spatial assessment of water quality parameters in Jhelum city (Pakistan). Environ. Monit. Assess. 189 (3), 119.

Jehan, S., Khattak, S., Muhammad, S., Ali, L., Luqman, M., 2020. Human health risks by potentially toxic metals in drinking water along the Hattar Industrial Estate, Pakistan. Environ. Sci. Pollut. Res. 27 (3), 2677–2690.

Jones, W.R., Spence, M.J., Bowman, A.W., Evers, L., Molinari, D.A., 2014. A software tool for the spatiotemporal analysis and reporting of groundwater monitoring data. Environ. Model Softw. 55, 242–249.

Kalyoncu, L., Kalyoncu, H., Arslan, G., 2012. Determination of heavy metals and metals levels in five fish species from Işıklı Dam Lake and Karacaören Dam Lake (Turkey). Environ. Monit. Assess. 184 (4), 2231–2235.

Kelepertzis, E., Galanos, E., Mitsis, I., 2013. Origin, mineral speciation and geochemical baseline mapping of Ni and Cr in agricultural topsoils of Thiva valley (Central Greece). J. Geochem. Explor. 125, 56–68.

Khalid, S., Shahid, M., Natasha., Shah, A,H., Dumat, C., 2020. Heavy metal contamination and exposure risk assessment via drinking groundwater in Vehari, Pakistan. Environ. Sci. Pollut. Res. 27(32), 1–13.

Khan, T., Muhammad, S., Khan, B., Khan, H., 2011. Investigating the levels of selected heavy metals in surface water of Shah Alam River (A tributary of River Kabul, Khyber Pakhtunkhwa). J. Himalayan Earth Sci. 44 (2), 71–79.

Khan, K., Lu, Y., Khan, H., Zakir, S., Ihsanullah., Khan, S., Khan, A.A., 2013a. Health risks associated with heavy metals in the drinking water of Swat, northern Pakistan. J. Environ. Sci. 25 (10), 2003–2013.

Khan, S., Shahnaz, M., Jehan, N., Rehman, S., Shah, M.T., Din, I., 2013b. Drinking water quality and human health risk in Charsadda district, Pakistan. J. Clean. Prod. 60, 93–101.

Khan, S., Shah, I.A., Muhammad, S., Malik, R.N., Shah, M.T., 2015. Arsenic and heavy metal concentrations in drinking water in Pakistan and risk assessment: a case study. Human and Ecological Risk Assessment: An Int. J. 21 (4), 1020–1031.

Koklu, R., Sengorur, B., Topal, B., 2010. Water quality assessment using multivariate statistical methods—a case study: Melen River System (Turkey). Water Resour. Manag. 24 (5), 959–978.

Kumpiene, J., Lagerkvist, A., Maurice, C., 2008. Stabilization of As, Cr, Cu, Pb and Zn in soil using amendments–a review. Waste Manag. 28 (1), 215–225.

Li, P., Wu, J., Qian, H., Lyu, X., Liu, H., 2014. Origin and assessment of groundwater pollution and associated health risk: a case study in an industrial park, Northwest China. Environ. Geochem. Health 36 (4), 693–712.

Lin, M., Gui, H., Peng, W., Chen, S., 2014. Heavy Metals Characteristics in Deep Groundwater of Coal Mining Area, Northern Anhui Province. In: Sui, W.H., Sun, Y.J., Wang, C.S. (Eds.), An Interdisciplinary Response to Mine Water Challenges. China University of Mining and Technology Press, Xuzhou.

Liu, Y., Ma, R., 2020. Human Health Risk Assessment of Heavy Metals in Groundwater in the Luan River Catchment within the North China Plain. Geofluids 2020, 8391793.

Lloyd, J.W., Heathcote, J., 1985. Natural Inorganic Hydrochemistry in Relation to Ground Water. Clarendon Press, Oxford.

Macklin, M.G., Klimek, K., 1992. Dispersal, storage and transformation of metalcontaminated alluvium in the upper Vistula basin, Southwest Poland. Appl. Geogr. 12 (1), 7–30.

Magesh, N., Krishnakumar, S., Chandrasekar, N., Soundranayagam, J.P., 2013. Groundwater quality assessment using WQI and GIS techniques, Dindigul district, Tamil Nadu, India. Arab. J. Geosci. 6 (11), 4179–4189.

Maity, S., Biswas, R., Sarkar, A., 2020. Comparative valuation of groundwater quality parameters in Bhojpur, Bihar for arsenic risk assessment. Chemosphere 259, 127398.

Majidano, S.A., Khuhawar, M.Y., 2009. Distribution of heavy metals in the ground water of Taluka Daur, District Nawabshah, Sindh, Pakistan, and its impacts on human health. J. Chem. Soc. Pak. 31 (3), 408–414.

McKnight, U.S., Finkel, M., 2013. A system dynamics model for the screening-level long-term assessment of human health risks at contaminated sites. Environ. Model Softw. 40, 35–50.

Mohamed, Z.A., Al Shehri, A.M., 2009. Microcystins in groundwater wells and their accumulation in vegetable plants irrigated with contaminated waters in Saudi Arabia. J. Hazard. Mater. 172 (1), 310–315.

Muhammad, S., Shah, M.T., Khan, S., 2011. Health risk assessment of heavy metals and their source apportionment in drinking water of Kohistan region, northern Pakistan. Microchem. J. 98 (2), 334–343.

Murasingh, S., Jha, R., Adamala, S., 2018. Geospatial technique for delineation of groundwater potential zones in mine and dense forest area using weighted index overlay technique. Groundw. Sustain. Dev. 7, 387–399.

Nas, B., 2009. Geostatistical Approach to Assessment of Spatial distribution of Groundwater Quality. Pol. J. Environ. Stud. 18 (6), 1073–1082.

Oke, A., Sangodoyin, A., Ogedengbe, K., Omodele, T., 2013. Mapping of river waterquality using inverse distance weighted interpolation in Ogun-Osun river basin, Nigeria. Acta Geographica Debrecina Landscape & Environ. 7 (2), 48–62.

Ponsadailakshmi, S., Sankari, S.G., Prasanna, S.M., Madhurambal, G., 2018. Evaluation of water quality suitability for drinking using drinking water quality index in Nagapattinam district, Tamil Nadu in Southern India. Groundw. Sustain. Dev. 6, 43–49.

Rani, R., Chaudhary, B., 2015. Spatial distribution Mapping and Assessment of Suitability of Groundwater Quality for Drinking Purpose in Hisar District of Haryana State, India. SSARSC Int. J. Geo-Sci. Geo-inform. 2 (1), 1–8.

Rashid, A., Guan, D.X., Farooqi, A., Khan, S., Zahir, S., Jehan, S., Khattak, S.A., Khan, M.S., Khan, R., 2018. Fluoride prevalence in groundwater around a fluorite mining area in the flood plain of the River Swat, Pakistan. Sci. Total Environ. 635, 203–215.

Rashid, A., Khan, S., Ayub, M., Sardar, T., Jehan, S., Zahir, S., Khan, M.S., Muhammad, J., Khan, R., Ali, A., Ullah, H., 2019a. Mapping human health risk from exposure to potential toxic metal contamination in groundwater of lower Dir, Pakistan: Application of multivariate and geographical information system. Chemosphere 225, 785–795.

Rashid, A., Khan, S., Ayub, M., Sardar, T., Jehan, S., Zahir, S., Khan, M.S., Muhammad, J., Khan, R., Ali, A., Ullah, H., 2019b. Mapping human health risk from exposure to potential toxic metal contamination in groundwater of lower Dir, Pakistan: application of multivariate and geographical information system. Chemosphere 225, 785–795.

Rashid, A., Khattak, S.A., Ali, A., Zaib, M., Jehan, S., Ayub, M., Ullah, H., 2019c. Geochemical profile and source identification of surface and groundwater pollution of District Chitral, Northern Pakistan. Microchem. J. 145, 1058–1065.

Rashid, A., Farooqi, A., Gao, X., Zahir, S., Khattak, J.A., 2020. Geochemical modeling, source apportionment, health risk exposure and control of higher fluoride in groundwater of sub-district Dargai, Pakistan. Chemosphere 243, 125409.

Ravindra, K., Mor, S., 2019. Distribution and health risk assessment of arsenic and selected heavy metals in Groundwater of Chandigarh, India. Environ. Pollut. 250, 820–830.

Ritter, L., Solomon, K., Sibley, P., Hall, K., Keen, P., Mattu, G., Linton, B., 2002. Sources, pathways, and relative risks of contaminants in surface water and groundwater: a perspective prepared for the Walkerton inquiry. J. Toxicol. Environ. Health Part A 65 (1), 1–142.

Saha, N., Rahman, M.S., Ahmed, M.B., Zhou, J.L., Ngo, H.H., Guo, W.S., 2017. Industrial metal pollution in water and probabilistic assessment of human health risk. J. Environ. Manag. 185, 70–78.

Saleh, H.N., Panahande, M., Yousefi, M., Asghari, F.B., Oliveri, C.G., Talaee, E., Mohammadi, A.A., 2019. Carcinogenic and non-carcinogenic risk assessment of heavy metals in groundwater wells in Neyshabur Plain, Iran. Biol. Trace Elem. Res. 190 (1), 251–261.

Salud, O.M.D.L., Suiza, Staff, W.H.O, 1997. Guidelines for Drinking-Water Quality: Surveillance and Control of Community Supplies, 3. World Health Organization.

Sari, A., Tuzen, M., 2008. Biosorption of total chromium from aqueous solution by red algae (Ceramium virgatum): equilibrium, kinetic and thermodynamic studies. J. Hazard. Mater. 160 (2–3), 349–355.

Shah, M., Tariq, S., 2006. Oxygen isotope chemistry of the water from Peshawar Basin, Pakistan. J. Chem. Soc. Pak. 28 (5), 494–500.

Shah, M., Ara, J., Muhammad, S., Khan, S., Tariq, S., 2012. Health risk assessment via surface water and sub-surface water consumption in the mafic and ultramafic terrain, Mohmand agency, northern Pakistan. J. Geochem. Explor. 118, 60–67.

Shah, M.T., Ara, J., Muhammad, S., 2014. Potential heavy metals accumulation of indigenous plant species along the mafic and ultramafic terrain in the Mohmand Agency, Pakistan. Clean–Soil, Air, Water: A J. Sustain. Environ. Safety 42 (3), 339–346.

Singh, A., Smith, L.S., Shrestha, S., Maden, N., 2014. Efficacy of arsenic filtration by Kanchan Arsenic Filter in Nepal. J. Water Health 12 (3), 596–599.

Singh, U.K., Ramanathan, A., Subramanian, V., 2018. Groundwater chemistry and human health risk assessment in the mining region of East Singhbhum, Jharkhand, India. Chemosphere 204, 501–513.

Soltani, N., Keshavarzi, B., Moore, F., Tavakol, T., Lahijanzadeh, A.R., Jaafarzadeh, N., Kermani, M., 2015. Ecological and human health hazards of heavy metals and polycyclic aromatic hydrocarbons (PAHs) in road dust of Isfahan metropolis, Iran. Sci. Total Environ. 505, 712–723.

Taşar, Ş., Kaya, F., Özer, A., 2014. Biosorption of lead (II) ions from aqueous solution by peanut shells: equilibrium, thermodynamic and kinetic studies. J. Environ. Chem. Eng. 2 (2), 1018–1026.

Webster, R., Oliver, M.A., 2007. Geostatistics for Environmental Scientists. John Wiley & Sons, pp. 1–315.

WHO, 2011. Guidelines for drinking water quality. WHO Chronicle 4 (38), 104–108.

Xu, B., Xu, Q., Liang, C., Li, L., Jiang, L., 2015. Occurrence and health risk assessment of trace heavy metals via groundwater in Shizhuyuan Polymetallic Mine in Chenzhou City, China. Front. Environ. Sci. & Eng. 9 (3), 482–493.

Zumlot, T., Batayneh, A., Nazal, Y., Ghrefat, H., Qaisy, S., 2013. Using multivariate statistical analyses to evaluate groundwater contamination in the northwestern part of Saudi Arabia. Environ. Earth Sci. 70 (7), 3277–3287.