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ORIGINAL PAPER

Unraveling prevalence and public health risks of arsenic, uranium and co-occurring trace metals in groundwater along riverine ecosystem in Sindh and Punjab, Pakistan

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Abstract The current study focuses on the understanding of contamination status, distribution, source apportionment and health perspectives of arsenic (As), uranium (U) and other co-occurring trace metals in the groundwater samples collected along the major rivers in Sindh and Punjab provinces, Pakistan. ICP-MS analysis revealed that the concentrations of As in the groundwater in Sindh and Punjab ranged from 0.2 to 81.1 μg/L (n = 38) and 1.1 to 501.1 μg/L (n = 110), respectively. Importantly, this study is the first evidence of U contamination in the groundwater samples in Pakistan, which revealed the concentrations of U at from 0.8 to 59.0 and 0.1 to 556.0 μg/L respectively, in Sindh and Punjab. Moreover, the concentrations of Sr and Mn exceeded the WHO limits in the current study area. Anthropogenic activities such as urbanization, direct dispose of industrial, agricultural waste into waterways and extensive use of pesticides and fertilizers might be the main sources of elevated levels of total dissolved solids and electrical conductivity, which increased the mobilization of As, U and Sr in the groundwater samples. Human health risk assessment parameters such as average daily dose, hazard quotient (HQ) and cancer risk indicated severe

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risks of As and U in the study area. The HQ values of As and U in Punjab were observed at 69.6 and 7.7, respectively, implying the severity of the health risks associated with consumption of contaminated groundwater for drinking purposes. In a nutshell, proactive control and rehabilitation measures are recommended to eradicate trace metals associated groundwater contamination in the targeted areas to avoid future worst scenarios.

Keywords Arsenic · Uranium · Groundwater · Health risk · Cancer risk · Pakistan

Introduction

As-contaminated groundwater is a serious threat for public health and a major environmental cause of cancer mediated mortality, worldwide (Pham et al. 2017). It has been estimated that more than 200 million people are consuming As-contaminated groundwater globally (Naujokas et al. 2013). In Southeast Asia, groundwater is the main source of drinking water and mostly preferred due to its stable state of good microbial quality (Chanpiwat et al. 2011; Ali et al. 2018a). Though in few cases, the natural water contains chemical elements that can have deleterious effects on human health (Liu et al. 2003). According to the UNICEF (UNICEF 2008), approximately 60 million residents in Southeast Asian countries are consuming As-contaminated groundwater for drinking and cooking purposes on daily basis. Unfortunately, around 700,000 individuals in this region are extremely affected with As-related illnesses such as black foot disease, arsenicosis, cardiovascular diseases and different types of cancer (Frisbie et al. 2002; Rahman et al. 2009).

The general mechanisms of As mobilization in groundwater is categorized as: reducing or oxidizing environmental conditions, weathering of sulfide-bearing minerals and geothermal activities (Nickson et al. 2000; Schreiber et al. 2000; Smedley and Kinniburgh 2002; Welch and Stollenwerk 2003). The common hydrological features in Southeast Asian countries (India, China, Bangladesh and Pakistan) are mainly included sedimentary and low-lying flat topographies, slow moving groundwater, fast Holocene sedimentation sustained by large rivers and existence of excess degradable organic matter (Ali et al. 2018b; Shakoor et al. 2018). The aquifers within Holocene deposits are mainly susceptible to As enhancement because these sediments hold abundance of mobilized As within the grains and are in contact with the groundwater flushing (Postma et al. 2012). The concentration of As also increased in areas with low hydrological gradients, resulting in slow groundwater flows, as well as arid environmental conditions that lead to evaporative concentration (Gao et al. 2007). The As concentrations in natural water exceeding the WHO drinking water reference concentration have been reported in different countries such as India, Pakistan, Bangladesh, China, Nepal, Vietnam, Mongolia, Myanmar, Cambodia, Indonesia, Morocco and Thailand (Berg et al. 2001; Frisbie et al. 2002; Chakraborti et al. 2003; Buschmann et al. 2007; Winkel et al. 2008; Luu et al. 2009; Pokhrel et al. 2009; Rahman et al. 2009; Moyé et al. 2017; Pham et al. 2017; Podgorski et al. 2017; Rasool et al. 2017). Due to the extensive water availability and high soil fertility, the Indus River plain in Pakistan witnessed a wide agronomic production that lead to the huge increase in population greater than 100 million individuals (Podgorski et al. 2017). Importantly, the unconfined aquifers in Pakistan originate along the Indus plain and are primarily consisted of 300 m of quaternary sedimentary deposits and porous soil with least organic content (Greenman et al. 1967). In the Indus plain, there is a strong association between the river water, wide irrigation system and low-lying aquifers (Farooqi et al. 2009). However, the morphology and the presence of old flat-lying Holocene fluvial deposits across the Indus River make it quite similar to those well-known As-affected regions of the Ganges River in Bangladesh as well as in India (Ravenscroft et al. 2009), the Red River in Vietnam (Berg et al. 2001) and the Mekong River in Vietnam and Cambodia (Chanpiwat et al. 2011).

Uranium (U) is ubiquitous in the atmosphere and is a non-essential element for humans, as it has no well-known metabolic function. The long-term exposure to U radionuclides in terms of groundwater consumption causes serious human health effects (Bajwa et al. 2017). The toxicity of U depends on various factors such as exposure route, exposure time and removal pathway (Brugge and Oldmixon 2005). The frequent intake of U, even in small quantities, may cause damage to kidneys, lungs, liver and cardiovascular system, and it also exhibits carcinogenic behavior as

radon decay byproduct (Buschmann et al. 2008; Chanpiwat et al. 2011). The varying concentrations of U and associated sources have been reported in groundwater of different countries worldwide such as Brazil, USA, Norway, Kuwait, Jorden, Turkey, Argentina, Iran, Germany, Sweden, Afghanistan, India and China (Table S1) (Geraldo et al. 1979; Cothern and Lappenbusch 1983; Banks et al. 1995; Bou-Rabee 1995; Gedeon et al. 1995; Kumru 1995; Bomben et al. 1996; Alirezazadeh and Garshasbi 2003; UNICEF 2008; Seldén et al. 2009; Kato et al. 2016; Bajwa et al. 2017; Wu et al. 2018). At present, no specific national standard is defined for U levels in drinking water in Pakistan.

The trace elements' mediated pollution in groundwater is one of the serious concerns all over the world, due to their perseverance, accumulation and environmental toxicity (Rasool et al. 2016a). However, the most common effects of oral exposure to excess Sr are reduced cartilage calcification and osteomalacia/decreased bone mineralization, especially in adults (Höllriegl and München 2011). Minute quantities of Mn are essential to human health. Mn also serves as a catalyst and cofactor in different enzymatic processes that involved in the synthesis of fatty acids and cholesterol. A high intake of Mn causes specific human health effects such as neural disorders, lungs and reproductive system failure and psychiatric and also movement disorders (Chanpiwat et al. 2011). In oxygen-depleted groundwater, soluble Mn is present in the form of Mn^{2+}, which shows moderate solubility (de Joode et al. 2016; Thuyet et al. 2016). The anthropogenic sources of trace elements include direct disposal of industrial waste in waterways (Muhammad et al. 2011) and widespread use of pesticides and fertilizers (Abbas et al. 2014). The natural water quality in most of the rivers, lakes and groundwater of the country is considered not to be safe for human drinking (Azizullah et al. 2011). While considerable studies have been conducted about As contamination, the distribution of trace elements and health effects are still not well defined along the major rivers. The main objective of the present study is to investigate the contamination status, distribution, associated human health risks of As, U and other trace element in the groundwater along the riverine ecosystem of two main provinces of Pakistan, namely Sindh and Punjab.

Materials and methods

Geological setting

More than 75% of the entire population of Pakistan reside in the two main provinces of Pakistan, that is, Sindh and Punjab. The study area is categorized by the flat-low-lying Indus plain (Fig. 1). The climate of the study area is semiarid to arid except for the temperate northwest, and this area is mainly composed of about 300 m of quaternary sedimentary deposits and porous soils with low organic content (Mushtaq et al. 2018). Unconsolidated sedimentary deposits of quaternary age are responsible for development of most aquifer systems along the major rivers of Sindh and Punjab (Podgorski et al. 2017). Though, unconfined aquifer is composed of sedimentary complex and alluvial sands with an average thickness of about 400 m (Ali et al. 2018b). The deposits are primarily consisted of fine to average sand, silt and clay with diverse extents of muscovite, quartz, biotite, chlorite and heavy minerals (Mushtaq et al. 2018). Due both to the heterogenic nature and the presence of sedimentary deposits, these aquifers are well known as homogeneous with very high transmissivity (Greenman et al. 1967). The key sources of groundwater recharge in the area include rainfall, the Indus River Ravi, the Chenab River, the Jhelum River, and the Sutlej River and widespread irrigation waterways (Eqani et al. 2016; Mushtaq et al. 2018).

Sample collection and preparation

In November 2017, a total of 148 groundwater samples were randomly collected from the pre-existing wells (with varying depths 27.1–61.1 m) that were located along riverine ecosystem in two main provinces of Sindh (n =38) and Punjab (n =110), Pakistan (Fig. 1). The collected samples were stored in 50-mL plastic (propylene) bottles at 4 °C by following the standard sampling protocols and methods defined by (APHA 2005). The samples collected for trace elemental analysis were filtered by using a 0.45-µm membrane (Whatman, USA), before preservation, and the samples were acidified with nitric acid (HNO_3) to lower the pH to < 2. All the samples were tightly capped, stored at dry ice conditions temperature up to 4 °C and transported to the "State Key Laboratory of Environmental Geochemistry, Chinese

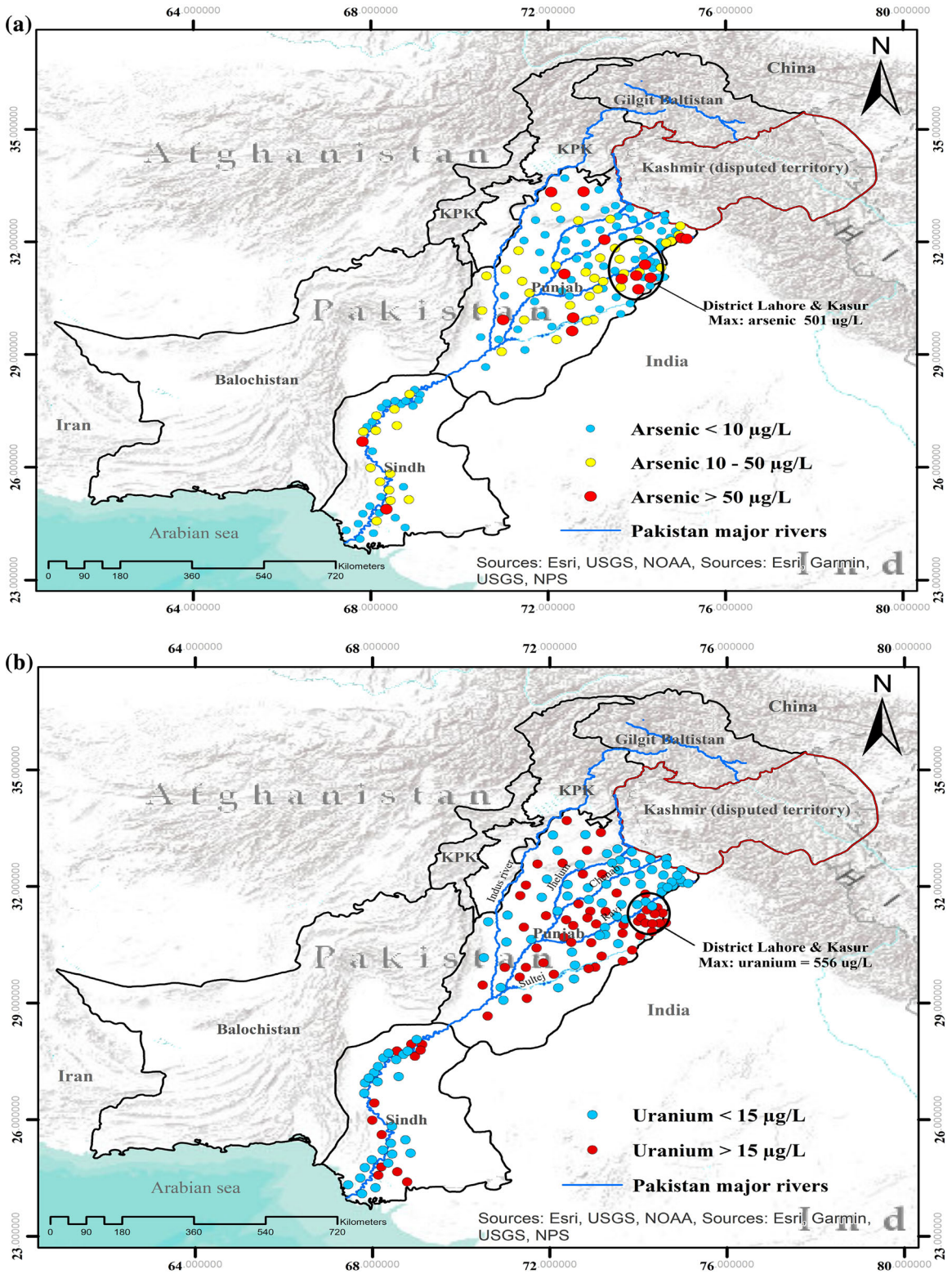

Fig. 1 Location maps showing the sampling points with As < 10, As 10–50, and As > 50 µg/L (**a**), U < 15 and U > 15 µg/L (**b**)

Academy of Sciences, Guiyang, China." To maintain and assure the quality and integrity of the samples, critical quality control measurements were also taken from the collected samples to analysis (detail presented in Sect. 1 of the Supplementary Information). The replicates of samples were also collected to reduce the cross-contamination during sampling, and all instruments were correctly calibrated before analysis.

pH, EC, TDS, color and trace element analysis

All the samples collected from different locations of the study area were clear and colorless. The pH and EC were measured in field using pH/EC meter (HANNA instruments, Canada), and electrodes were properly calibrated before sample analysis. Most of the samples had pH level in the range typical for drinking water about 6.5–8.5, as recommended by WHO. The TDS were also measured indirectly by using EC values and conversion factor defined by Moharir et al. (2002) in the following equation:

$$\text{TDS (mg/L)} = \text{EC } (\mu\text{S/cm}) \times 0.64 \quad (1)$$

The dissolved trace elements including cadmium (Cd), cobalt (Co), chromium (Cr), copper (Cu), iron (Fe), gallium (Ga), manganese (Mn), nickel (Ni), plumbum (Pb), rubidium (Rb), selenium (Se), strontium (Sr), thallium (Tl), vanadium (V), zinc (Zn), barium (Ba) and uranium (U) were measured in the groundwater samples by using inductively coupled plasma mass spectrometry (ICP-MS) (Agilent 7700×, California, USA). During the trace element analysis, blank and two standard reference material (SRM1640a) purchased from National Institute of Standards and Technology (NIST, USA) for water samples were also analyzed after each 10th sample. The measurement of uncertainties for all constraints was measured and controlled by using a regular laboratory replica of samples and confirming the precision/calibration of the instrument over regular runs with standard solutions. The recoveries of analytes of interest were in the range of 98.2–105.5%, and recovery of the SRM 1640a was ranged between 89.5 and 112.9%.

Health risk assessment

The human health risk assessment was based on the human exposure pathway: the groundwater to human via direct consumption of drinking water. The human health effects of As and U ingestion through drinking water are divided into two types: cancer-causing and non-cancer-causing effects. In the present study, the methodology adopted in permeant resident adults' receptor for assessment of cancer risk and chemical toxicity of As and U in groundwater samples is described below.

The chemical toxicity or non-carcinogenic health risks of trace elements were calculated in terms of the average daily dose (ADD) of the element via consumption of drinking water. The observed contact point level in (μg/L) of a specified contaminant, which is the ADD of a chemical substance ingested per/kg of body weight/day, is specified in the following equation (Rasool et al. 2016b; Bajwa et al. 2017; Barzegar et al. 2018).

$$\text{ADD} = \frac{C \times \text{IR} \times \text{ED} \times \text{EF}}{\text{BW} \times \text{AT} \times 365} \quad (2)$$

where C is the concentration of the target pollutant in the environmental comportment (mg/L or mg/kg), IR is the intake rate/unit time (3 mg/day or 3 L/day), ED in the exposure duration (65 years), EF is the exposure frequency (365 days/year), BW is the average body weight of the permeant resident adults receptor, i.e., 72 kg, and AT is average time/years, which is equal to average life expectancy 65 years and is multiplied by 365 to change the factors from years to days. The toxic risk is the non-carcinogenic harm sustained due to exposure (Islam et al. 2018), and the extent of harm is indicated in terms of the hazard quotient (HQ) (USEPA 1986);

$$\text{HQ} = \frac{\text{ADD}}{\text{RfD}} \quad (3)$$

where RfD is reference dose in daily intake that allows an exposed individual to tolerate this level of contact over an extended time without suffering any adverse effects (Saddique et al. 2018). The oral reference doses of As and U are 0.3 μg/kg and 3.0 μg/kg, respectively (Bajwa et al. 2017; Tabassum et al. 2018). The safe level of the HQ is < 1.0 for U and As (Rasool et al. 2016c; Bajwa et al. 2017). The cancer risk or carcinogenic risk (CR) in permeant resident adults was calculated by using the following equation:

$$\text{CR} = \text{ADD} \times \text{CSF} \quad (4)$$

where CSF is the cancer slope factor for As and U, 1.5 and 1.19 mg/kg/day, respectively (Bajwa et al. 2017; Tabassum et al. 2018).

Geological maps and multivariate analysis

The geological maps of the study area were developed using ArcGIS 10.3 (ESRI, USA), and the kriging interpolation method was applied to estimate the distribution of trace elements in the study area. The kriging interpolation technique is a standard practice that is mostly used for estimation of contaminants' regional distribution in the study area and is often used in hydrological studies (Gaus et al. 2003). The multivariate statistical analysis was performed using XLSTAT (Addinsoft, USA) and SPSS 20 software (IBM, USA). The principal component analysis (PCA) for source apportionment of the physiochemical parameters was extracted by using the multivariate statistical package software (MVSP). The PCA is primarily carried out by the diagonalization of an association matrix; thus, the problems that arise from the several numerical ranges of the original variables in the dataset are avoided, and all variables in the dataset are automatically scaled with the variance unit and similarly contributed (Jackson 2005).

Results and discussion

Physicochemical parameters

The physicochemical parameters (well depth, pH, EC, TDS) of the groundwater samples are shown in (Table 1). The groundwater samples were collected from different depths ranging from 27.1 to 61.1 m and 30.1 to 61.1 m in Sindh and Punjab, respectively. The samples from Sindh and Punjab had neutral to alkaline pH values ranging from 7.3 to 8.7 and 7.1 to 9.0, respectively (average = 7.9, SD = 0.4); 13.0% of the samples from Sindh and 4.5% of the samples from Punjab were exceeding the WHO pH standard. The EC and TDS values in Sindh varied from 657.0 to 3582.0 µS/cm and 440.0 to 2400.0 mg/L, respectively (average = 1492.0 µS/cm, SD = 707.0 µS/cm, average = 999.0 mg/L, SD = 474.0 mg/L), and in Punjab, these values ranged from 313.0 to 13,284.0 µS/cm and 210.0 to 8900.0 mg/L, respectively

Table 1 Physicochemical parameters values of well depth, pH, EC and TDS and in all groundwater, sample collected along riverine ecosystem in Sindh and Punjab, Pakistan

Parameters	Units	WHO limit	Sindh (n = 38)					Punjab (n = 110)				
			Minimum	Maximum	Average	Standard deviation (SD)	% n exceeding WHO limit	Minimum	Maximum	Average	Standard deviation (SD)	% n exceeding WHO limit
Well depth	m	–	27.1	61.1	35.1	7.1	–	30.1	61.1	48.0	8.0	–
pH	–	6.5–8.5	7.3	8.7	7.9	0.4	13.0%	7.1	9.0	7.9	0.4	4.5%
EC	µS/cm	1500	657.0	3582.0	1492.0	707.0	37.0%	313	13,284.0	1217.0	1369.0	15.4%
TDS	mg/L	< 1000	440.0	2400.0	999.0	474.0	37.0%	210	8900.0	815.0	917.0	15.4%

Number of samples (n)

(average = 1217.0 µS/cm, SD = 1369.0 µS/cm, average = 815.0 mg/L, SD = 917.0 mg/L). A total of 37.0% and 15.4% of the samples from Sindh and Punjab had concentrations exceeding the WHO guideline values of 1500 µS/cm and 1000 mg/L, respectively. The EC is an indicator of the salt content in the drinking water in the form of major ions (Laluraj and Gopinath 2006). These conductive ions naturally come from dissolved salts and inorganic materials such as alkalis, chlorides, sulfides and carbonate compounds (Arumugam and Elangovan 2009; INC 2016). The ions enter to the aquifer due to waste leakage or dissolution of rocks (Marghade et al. 2012). The EC value of the groundwater similarly depends upon recharge from river/waterway, rainfall or irrigation returns. In the present study, the regions with high EC might be polluted due to the direct disposal of industrial and other wastewater into rivers, and irrigation returns (Azizullah et al. 2011; Hanif et al. 2016), whereas the areas with low EC may be recharged by waterways or any fresh canals that pass adjacent. The similar type of findings was also reported in Sindh and Punjab in previous studies (Nickson et al. 2005; Brahman et al. 2013; Abbas et al. 2014; Rasool et al. 2016a; Podgorski et al. 2017). The elevated level of EC in different areas may be due to high levels of TDS, and there may be specific cations and anions in these areas. Likewise, the elevated levels of EC in groundwater samples were attributed to the occurrence of high concentration of dissolved solids in the previous studies (Ahdullah et al. 1999; Farooqi et al. 2009; Rasool et al. 2016a). The TDS values from the current study were consistent to those reported in different studies carried out previously in Sindh and Punjab regions, whereas the values of TDS in some regions were found above the acceptable limits of WHO (Kazi et al. 2009; Abbas et al. 2014). The elevated concentration of TDS in the samples may be attributed to the dissolution or mineralization of organic and inorganic contents in aquifers (Mohsin et al. 2013).

Arsenic and uranium distribution in groundwater

The total As concentration measured in groundwater samples is summarized in (Table 2). Overall, the As concentration ranged from 0.2 to 501.1 µg/L (average = 20.4 µg/L, SD = 47.0 µg/L) and approximately 42.0% of all 148 samples had As level higher than

Table 2 Trace element concentration of As, U, Sr, Mn and Rb exceeding the WHO permissible limit in all groundwater samples collected along riverine ecosystem in Sindh and Punjab, Pakistan

Parameters	Units	WHO limit	Sindh (n = 38)					Punjab (n = 110)				
			Minimum	Maximum	Average	Standard deviation (SD)	% n exceeding WHO limit	Minimum	Maximum	Average	Standard deviation (SD)	% n exceeding WHO limit (%)
As	µg/L	10	0.2	81.1	12.1	18.1	39.5%	1.1	501.1	23.1	53.0	43.1
U	µg/L	15	0.8	59.0	14.0	11.0	32.0%	0.1	556.0	29.5	61.0	41.0
Sr	µg/L	70	411.0	7137.1	1476.1	1134.1	92.1%	101.1	9962.1	906.1	955.1	100
Mn	µg/L	400	0.4	474.1	114.1	127.1	2.6%	0.1	1954.1	132.1	268.1	8.1
Rb	µg/L	10	0.5	2.5	1.3	0.5	–	0.2	11.6	2.1	1.7	1.0

Number of samples (n)

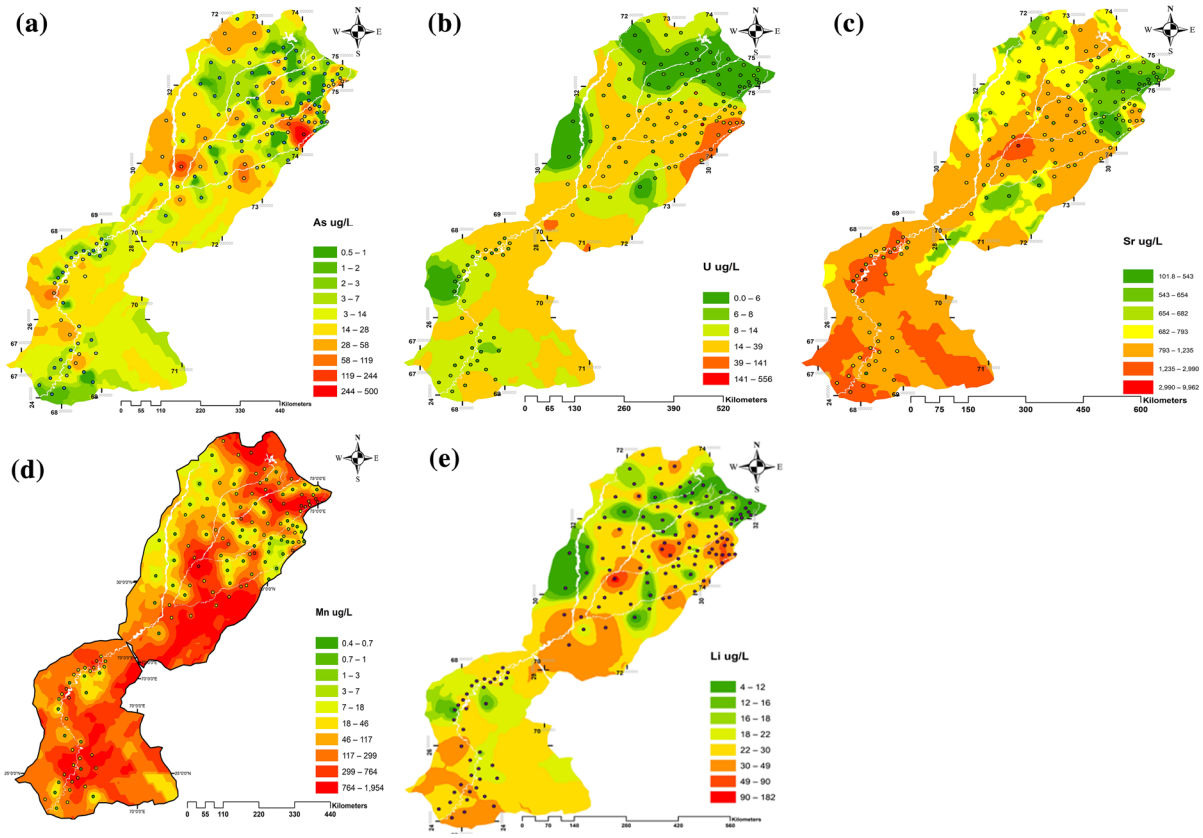

Fig. 2 Kriging estimated maps of trace elements As (**a**), U (**b**), Sr (**c**), Mn (**d**) and Li (**e**)

WHO standard 10 µg/L. In Sindh, the As concentration ranged from 0.2 to 81.1 µg/L (average = 12.1 µg/L, SD = 18.1 µg/L) and approximately 39.5% and 5.6% of all 38 samples had As concentrations exceeding the WHO guidelines and Pakistan National Environmental Quality Standards (Pak-NEQS) for As in drinking water, i.e., 10 and 50 µg/L, respectively. In Punjab, the total As concentrations ranged from 1.1 to 501.1 µg/L (average = 23.1 µg/L, SD = 53.0 µg/L) and approximately 43.1% and 12.7% of the 110 samples had the As concentrations exceeding the WHO-defined guideline and Pak-NEQS, respectively. The maximum As concentration of 501.1 µg/L was recorded in the Lahore region of Punjab. Arsenic is present in the form of compounds in groundwater and is usually absorbed onto the clay colloids bound with organic matter and forms the water-soluble complexes (Giacomino et al. 2010; Ali et al. 2018b). The previous evidence suggested that the geological distribution of As within alluvium sediments and various anthropogenic activities are responsible As mobilization is mediated through organic matter dissolution (Pal and Mukherjee 2009). The presence of As-loaded aquifers is mainly due to marine sedimentary rocks, weathering of volcanic rocks, inorganic mineral deposits, mining wastes, agricultural runoff and irrigation practices (Hunt and Howard 1994; Mondal et al. 2010b). The spatial distribution of As contamination in Sindh and Punjab (Fig. 2a) revealed an increasing trend in As concentration from south to east toward the Indus Plain and the region between the Ravi River and the Chenab River. Lahore and Kasur districts were severely contaminated as the maximum As concentration measured was at 501.1 µg/L. However, an analysis of the sampling points with As > 10 µg/L revealed that reducing conditions are not prevailing in the present study area. Further, the fact that the total dissolved Fe concentrations were below the detection limit confirms that the oxidizing conditions prevailed in the current study area. The percentage of the area with values of As > 10 µg/L expressed a strong correlation with the elevated pH values that is

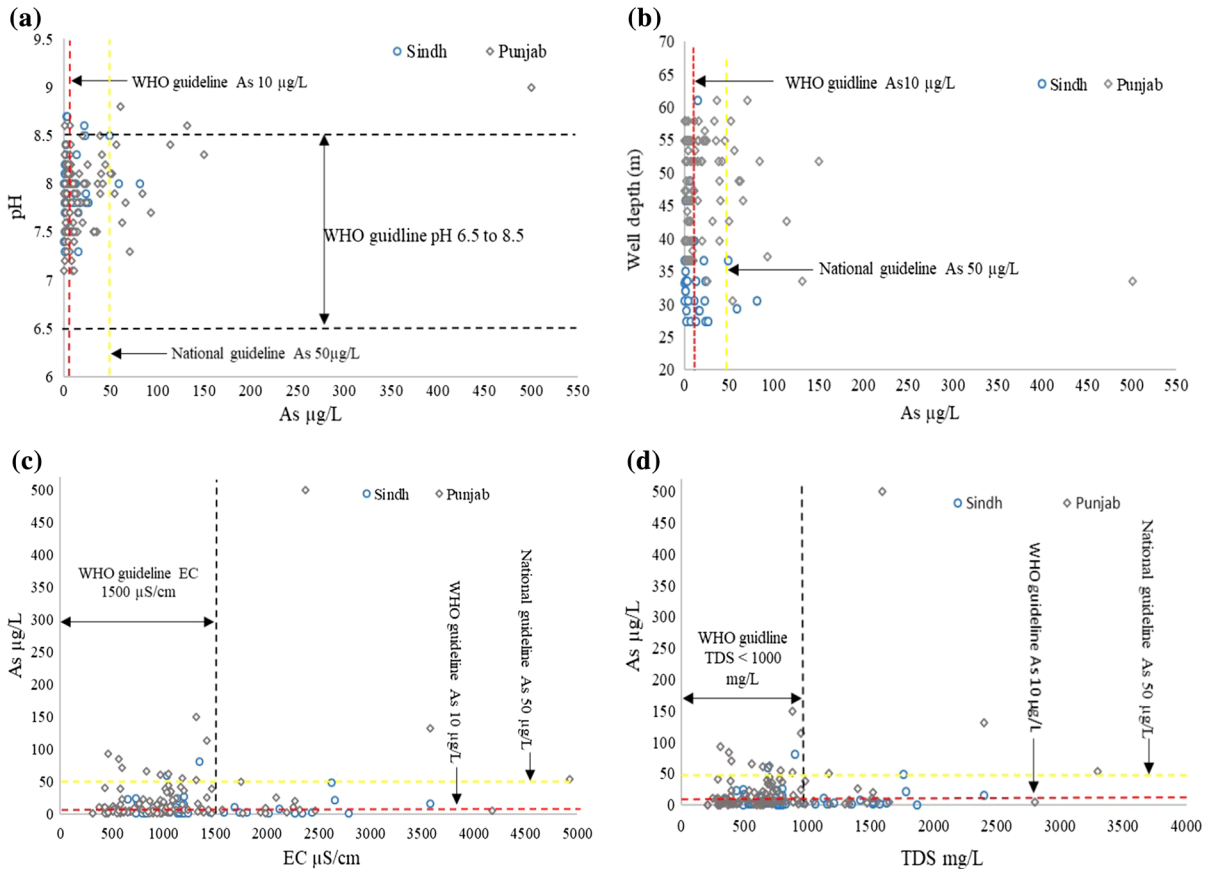

Fig. 3 Bivariate plots of As concentrations in groundwater with: pH (**a**) Well depth (**b**), EC (**c**) and TDS (**d**)

naturally observed high throughout the Indus Plain region. These results implied the pH-mediated desorption of As, consistent with findings previously reported by Farooqi et al. (2009), Rasool et al. (2015), Khalid et al. (2018) and Mushtaq et al. (2018). The pH values throughout the study areas in Punjab and Sindh are generally between 7.1 and 9.0, and the pH values of the samples (Fig. 3a) with As concentrations > 10 µg/l exhibited no significant correlation with As (Table S2). These findings indicated that As release due to high pH might be mainly occurred in the uppermost deposits prior to the transportation of As down through infiltration to the groundwater. The depth of the well was not correlated with As concentration, as the bivariate plot between As and well depth showed that As > 10 µg/L were dominant throughout the range of available well depth from 30.1 to 61.1 m, while the high As concentrations were found at well depths lower than 27.1 to 35.0 m (Fig. 3b). However, the highest As concentrations were dominant in areas with elevated EC and TDS concentrations (Fig. 3c, d).

Rainfall in arid areas is also strongly correlated with high As concentrations, which is strongly associated with the evaporation process in Sindh and Punjab, as suggested by Brahman et al. (2013) and Rasool et al. (2016c). The latter study found a prevalence of As (V) species associated with the reduced As (III) species (Donner et al. 2017). However, our current findings are more favorable for As release caused by oxidizing conditions or high pH dissolution, as the process of reductive dissolution in the region is primarily responsible for As release in the region. The reducing condition mainly is prevailed due to the organic waste generation from anthropogenic and natural sources in the urban areas (Nickson et al. 2005) or intense agricultural activities (Podgorski et al. 2017). Additionally, in the present study, we rarely observed a comparable basic pH and very low Fe concentrations in the tube well water along the

main rivers of Sindh and Punjab, Pakistan, thus indicating that As release might be geogenic and mainly related to reductive dissolution, as described in the previous studies (Hasan et al. 2009; Shakoor et al. 2018).

The concentration of U in Sindh ranged from 0.8 to 59.0 µg/L (average = 14.0 µg/L, SD = 11.0 µg/L), and results showed that approximately 32.0% of the samples from Sindh exceeded the WHO drinking water guidelines for U (15 µg/L). However, in Punjab the concentrations of U ranged from 0.1 to 556.0 µg/L (average = 29.5 µg/L, SD = 61.0 µg/L) and 41.0% of the samples from Punjab are exceeding the WHO limits. The maximum U concentration of 556.0 µg/L was reported in the groundwater samples from the Lahore district in Punjab (Fig. 1b). The results indicated that the average U level of 29.5 µg/L in groundwater can cause serious human health risks in Lahore and Kasur, Punjab province, because the most people regardless of age and sex consume groundwater water on daily basis. The kriging map (Fig. 2b) estimated that the higher concentrations of U were dominant in the southeast region along the India–Pakistan border. However, on the other side of the Pakistan border, a similar study was conducted by Bajwa et al. (2017) in the district of Indian–Punjab and reported that the U level ranged from 0.5 to 579.0 µg/L in groundwater. The possible sources of U in groundwater water may be associated with the leakage of U from adjoining basement with granite-rich rock formations. The anthropogenic activities, urbanizations and widespread use of pesticides and fertilizers are the main causes for the increase in the TDS level in groundwater, which may consequently lead to the high concentrations of U in aquifer (Bajwa et al. 2017). However, the current study showed no correlation between U concentration and TDS. The high concentration of U in the region may be due to geogenic or extensive use of fertilizers or pesticides and direct dispose of industrial waste into waterways. Further investigations are required to evaluate the sources and mobilization of U in drinking water. For comparison purposes, the concentration and possible sources U reported in the drinking water throughout the world are summarized in Table S1.

Elevated strontium and manganese in groundwater

Strontium (Sr) is ubiquitous in the environment and present in nearly all kinds of rocks and soils (Höllriegl and München 2011; Ruhl et al. 2014). The mean concentration of Sr in soil is about 240 mg/g (Höllriegl and München 2011). However, agricultural areas may contain more than 600 mg/g if treated with phosphate fertilizer or limestone (Höllriegl and München 2011). The release of Sr from earth crust into the environment takes place through natural processes such as the entrainment of dust particles, resuspension of soil through wind, and sea spray. Moreover, anthropogenic events, including milling and processing of Sr compounds, coal burning, extensive land application of phosphate fertilizers, and the usage of pyrotechnic devices, all enhance Sr contamination in the environment (Anke 2004; Höllriegl and München 2011). In Sindh, concentrations of Sr ranged from 411.0 to 7137.1 µg/L (average = 1476.1 µg/L, SD = 1134.1 µg/L) and 92.1% of the samples were exceeding the WHO limit for Sr in drinking water 70 µg/L. In Punjab, Sr ranged from 101.1 to 9962.1 µg/L (average = 906.1 µg/L, SD = 955.1 µg/L) and 100% of the samples from Punjab were exceeding WHO limit. The kriging estimate map (Fig. 2c) indicated the maximum concentrations were observed along coastal aquifers, and there were strong positive correlations between Sr versus TDS and EC (Table S2), which implied that the seawater intrusion was a significant source of Sr in groundwater (Mondal et al. 2010b). However, in Punjab, the high Sr was due to agricultural activities, extensive use of phosphate fertilizers and direct disposal of industrial wastewater into waterways, and aquifer recharge with contaminated water. According to Höllriegl and München (2011), the high intake of Sr content in drinking water > 400 µg/L can interrupt bone mineralization, which may result in lower bone mineral density, reduce the size of bone apatite and decrease calcium level, while alkaline and oxidizing conditions promote oxidation of soluble Mn^{2+} to insoluble forms of Mn-oxyhydroxides such as Mn_2O_3, MnOOH and MnO_x (Tebo et al. 2005; Mora et al. 2017). The results from present study indicated the high concentrations of Mn in the groundwater collected from each tested province. About 10.6% of the samples were exceeding the WHO limit for Mn in drinking water (400 µg/L). In Sindh and Punjab, the concentrations of Mn ranged from 0.4

to 474.1 µg/L (average = 114.1 µg/L, SD = 127.1 µg/L) and 0.1 to 1954.1 µg/L (average = 132.1 µg/L, SD = 268.1 µg/L), and 2.6% and 8.1% of samples, respectively, exceeded WHO guidelines 400 µg/L in groundwater. The estimates in the kriging map (Fig. 2d) indicated that most of Sindh and the southeast region of Punjab were contaminated with Mn.

Status of other trace elements pollution in groundwater

The concentrations of all other target trace elements are shown in (Table S3). Lithium (Li) as a trace element is naturally present in vegetables, grains and drinking water (Ohgami et al. 2009; Huthwaite and Stanley 2010). Nutritional studies have suggested that Li is an essential trace element with a recommended daily intake of 1 mg/day (Liaugaudaite et al. 2017). According to Zarse et al. (2011), the natural availability of Li in drinking water may increase the human lifespan. The current study revealed the concentrations of Li ranged from 4.0 to 182.0 µg/L (average = 25.0 µg/L, SD = 22.0 µg/L) in Sindh and from 8.0 to 45.0 µg/L (average = 23.0 µg/L, SD = 18.0 µg/L) in Punjab. So far, a recommended limit of Li in drinking water has not been set by the WHO. Figure 2e shows high concentrations of Li in the Lahore City of Punjab. Among all target analytes, Rb concentrations in the drinking water found almost within the limits recommended by the WHO 10 µg/L ranged from 0.2 to 11.6 µg/L (average = 2.1 µg/L, SD = 1.7 µg/L) and 1.0% of samples exceeded WHO guidelines. However, the concentrations of Cd, Co, Cr, Cu, Cs, Ni, Sb, V and Zn in all samples from both Sindh and Punjab were also within limits recommended by the WHO. The concentrations of Ga, Be, Se, Tl and Fe were found below detection limit (BDL), both in Punjab and Sindh.

Principal component analysis

The PCA results of the present study are summarized in Table S4, including the principal components loadings and eigenvalues of each principal cofactor. Different criteria are used to identify the numbers of components retained to recognize the underlying overall data structure (Jackson 2005). In the present study, the principal cofactors with eigenvalues > 1 were considered. By following this rule, five independent principal components (PC-1, PC-2, PC-3, PC-4 and PC-5) were extracted that explain 59.2% of the total population variance. The PC-1 explains 21.6% of the total variance and has high loadings. The PC-1 explains the strong positive correlation between EC, TDS, Li, Sr, Co, U and Mn. The strong positive correlation between EC, TD and Sr that again confirmed seawater intrusion, agricultural activities, extensive use of phosphate fertilizers and direct disposal of industrial wastewater into waterways might be a significant source of Sr in groundwater. The PC-2 explains 16.2% of the total dataset variance and mainly reflects the contributions of the positive correlation between As, pH, Cd and Mo (Fig. 4). The PC-2 describes the redox controls on the overall variability of As in groundwater, PC-3 explains 12.7% of the total data variance and is primarily associated with high factor loadings for Sb and V, whereas PC-4 and PC-5 explain 4.8% and 3.9% of the total data variance mainly linked with Ba, Rb and Cu, Zn, respectively.

Arsenic and uranium health risk assessment

There are several exposure pathways associated with the trace elements, mostly dependent on pollution medium such as water, soil, air, food and exposed population. However, among these pathways, the exposure via drinking contaminated water is a critical pathway for trace elements to enter human body (Caussy et al. 2003; Muchuweti et al. 2006). In the current study, the mean ADD values of As and U in Sindh and Punjab ranged from 0.1 to 3.4 µg/kg/day (average = 0.5 µg/kg/day), 0.3 to 2.5 µg/kg/day (average = 0.6 µg/kg/day) and 0.1 to 20.8 µg/kg/day (average = 1.1), 0.1 to 23.2 µg/kg/day (average = 1.2 µg/kg/day), respectively, (Table 3). The HQ values of As and U in Sindh and Punjab ranged from 0.1 to 11.2 (average = 1.7) and 0.1 to 0.8 (average = 0.2) and 0.2 to 69.6 (average = 3.2) and 0.1 to 7.7 (average = 0.4), respectively. However, these HQ values of As lower than those previously reported in groundwater samples (ranged from 1.13 to 41.7) from Mailsi, Punjab, Pakistan (Rasool et al. 2017). The CR values of As and U in Sindh and Punjab groundwater samples ranged from 0.2 to 5.1×10^{-3} (average = 7.5×10^{-5}) and 3.9×10^{-4} to 2.9×10^{-3} (average = 6.9×10^{-4}) and 6.2×10^{-5}

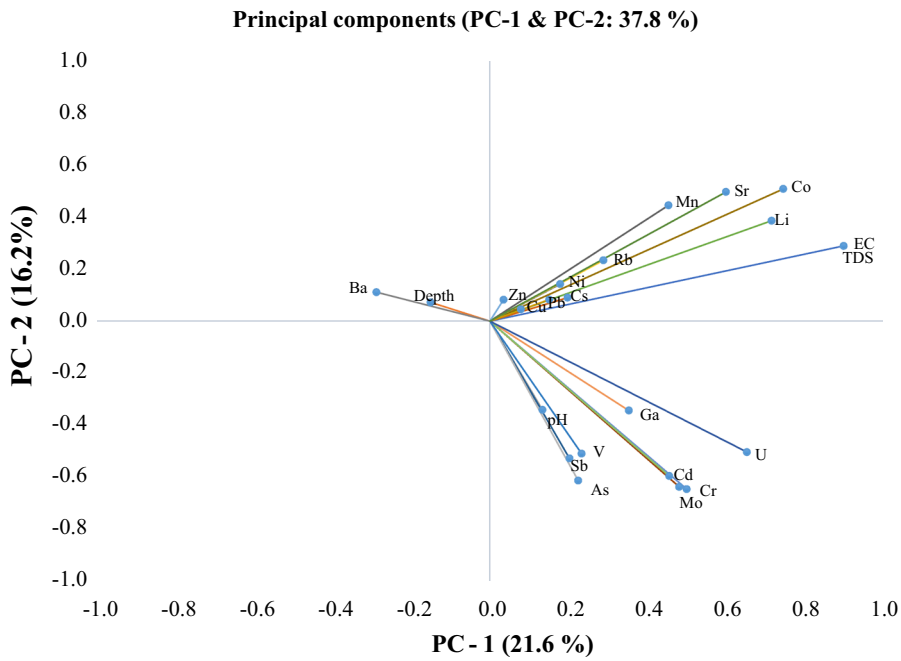

Fig. 4 Principal component analysis (PCA) showing the relationship between principal components (PC-1 and PC-2) indicating distribution/grouping of trace elements As, U, Sr and various other trace elements measured in groundwater along riverine ecosystem of Pakistan

Table 3 Summary of As and U concentrations corresponding to cancer risk (CR), average daily dose (ADD) and hazard quotient (HQ) for all groundwater along riverine ecosystem in Sindh and Punjab, Pakistan

Locations	Parameters	CR minimum–maximum and average	ADD minimum–maximum and average (μg/kg/day)	HQ minimum–maximum and average
Sindh $n = 38$	As	$0.2–5.1 \times 10^{-3}$ and 7.5×10^{-5}	0.1–3.4 and 0.5	0.1–11.2 and 1.7
	U	3.9×10^{-4}–2.9×10^{-3} and 6.9×10^{-4}	0.3–2.5 and 0.6	0.1–0.8 and 0.2
Punjab $n = 110$	As	6.2×10^{-5}–3.1×10^{-2} and 1.4×10^{-3}	0.1–20.8 and 1.1	0.2–69.6 and 3.2
	U	3.5×10^{-6}–2.8×10^{-2} and 1.5×10^{-3}	0.1–23.2 and 1.2	0.1–7.7 and 0.4

Number of samples (n)

to 3.1×10^{-2} (average = 1.4×10^{-3}) and 3.5×10^{-6} to 2.8×10^{-2} (average = 1.5×10^{-3}), respectively. In the present study area, the CR value of As exceeded those previously reported, i.e., 2.6×10^{-6} and 4.56×10^{-4} in groundwater samples from Ubon Ratchathani province, Thailand, and west Bengal, India, respectively (Mondal et al. 2010b; Wongsasuluk et al. 2014). The ADD, HQ, and CR values of As and U for exposed population in Punjab residing along riverine ecosystem of present study area locations were much higher than the safety limits. Therefore, on the basis of these findings, the groundwater of district Lahore and Kasur, Punjab, Pakistan, is more contaminated and not suitable for drinking purposes in comparison with that of Sindh.

Conclusion and recommendations

The current study revealed groundwater pollution mediated by As, U, Mn, Li and Sr prevailing in several areas along major rivers of two central provinces of Pakistan, Sindh and Punjab. These contaminants were especially present in the middle and eastern regions of

the country. In Sindh, 39.5%, 32.0% and 92.1% of the samples containing As, U and Sr concentrations exceeded the WHO-defined guidelines for drinking water (10, 15 and 70 µg/L), while 43.1%, 41.0% and 100% of the samples from Punjab exceeded these limits, respectively. Alkaline pH and very low Fe concentrations indicating oxidizing conditions prevailed in both Sindh and Punjab. As release in environment due to high pH desorption mainly occured in the uppermost deposits before being transported downward through infiltration to the groundwater. Moreover, the highest As concentrations were dominant in areas with elevated EC and TDS values, which indicated that salination, agricultural activities and the direct disposal of industrial waste into the riverine system contributed to As release into groundwater. The PCA revealed positive correlation between As and pH, which described the redox controls on the overall variability of arsenic in groundwater. Most noteworthy, the elevated concentrations of U in the groundwater samples were observed and this was the first evidence of U contamination in the aquifers of Pakistan. Strong positive correlations among Sr, TDS and EC revealed that seawater intrusion, extensive use of phosphate fertilizers and direct disposal of industrial wastewater into waterways are significant sources of Sr in groundwater. Health risk assessment parameters ADD, HQ and CR indicated severe risks of As and U occur in the sampling locations of the current study area. The HQ values of As and U in Punjab reached 69.6 and 7.7, respectively, which indicate the severity of the health risks associated with the use of As and U polluted groundwater for drinking purposes. However, further in-depth research must be conducted as to follow-up on the present study, with specific regard to the mobilization mechanisms and sources of As, U and other elements in the groundwater. Within another sphere, the synergistic and antagonistic health effects of As, U, Mn and Sr should be observed as to determine the cancer risks posed to population in Sindh and Punjab.

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Compliance with ethical standards

Conflict of interest The authors have no conflict of interest.

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