Chapter 24
Arsenic Contamination of Groundwater in Indus River Basin of Pakistan

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Abstract Arsenic (As) contamination of drinking water from groundwater sources is an issue of public health concern in many parts of the world, including South Asia. The presence of As in groundwater of Pakistan was reported around the city of Karachi as early as 1997. Widespread occurrences of As are reported in groundwater through a number of subsequent studies in the provinces of Punjab and Sindh, the two most populated provinces in the Indus River basin of Pakistan and thereby emerged as an issue of public health concern. These studies have revealed that concentrations of As are elevated by a factor of 10–250 as compared to the WHO drinking water guideline. Both natural and anthropogenic processes have been primarily indicated as cause for elevated As concentration in groundwater. An increasing number of studies also show evidence that irrigation with As contaminated groundwater is associated with elevated As concentrations in agricultural products. The future research should therefore focus on the detailed understanding of the complexities of the geological and hydrogeological setting of Pakistan and to outline the sources of As and the mechanisms of transport to the Indus basin aquifers.

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24.1 Introduction

Arsenic (As), a known carcinogen, occurs as a natural element in the Earth's crust. It is the 20th most abundant element in the upper crust with concentrations ranging between 1 and 2 mg/kg (Pontius et al. 1994). Emissions of As in the environment may be caused through both natural and anthropogenic processes (Borba et al. 2003; Gunduz et al. 2010; MacDonald et al. 2016; Marszałek and Wąsik 2000; Woo and Choi 2001). In aqueous environments, As can exist both in inorganic and organic forms, though in natural waters the former generally predominates (Pontius et al. 1994; Smedley and Kinniburgh 2002). Redox potential (E_h) and pH strongly control As speciation in aqueous environments (Mohan and Pittman 2007; Pontius et al. 1994; Smedley and Kinniburgh 2002; Wang and Mulligan 2006). Depending upon the redox condition, inorganic As can exist in two oxidation states: arsenite [As(III)] and arsenate [As(V)]. Arsenite [As(III)] mainly occurs under reducing conditions, e.g., in alluvial aquifers with abundant organic matter, whereas As(V) occurs mainly in well-oxidized systems. Since redox kinetics of As is generally slow in the presence of oxygen alone, both forms may also exist together.

Geogenic As contamination of drinking water from groundwater sources is an issue of public health concern in many parts of the world, including a major part of South Asia (Nriagu et al. 2007). The presence of As in groundwater of Pakistan (Chap. 1, Fig. 1.1) has been recognized as an issue of immediate public health concern. Many studies have reported correlation of elevated As concentration in drinking water (or food) to the observed negative effects on human health in Pakistan (Abbas et al. 2012; Afridi et al. 2011a, b, c; Baig et al. 2011b, c; Fatmi et al. 2009, 2013; Kazi et al. 2009, 2011; Nafees et al. 2011; Wadhwa et al. 2011a, b). The issue is not highlighted extensively in international scientific literature compared to the neighboring countries, e.g., Bangladesh and India. Thus, in this chapter, we aim to present a brief overview of the current status of As contamination in groundwater in different parts of the Indus River basin of Pakistan. More related information regarding groundwater of South Asia is available in Mukherjee (2018).

24.2 The Indus River Basin of Pakistan

Pakistan forms the western part of the Asian subcontinent with a land area of 0.7961 million km^2. It is located between the latitudes of 24° to 37°N and latitudes of 61° to 76°E. The country extends for 1700 km in the NE–SW direction while the E–W breadth is about 1000 km with a diverse mosaic of landforms formed by diverse geological setting comprising orogenic belt, sedimentary basins, magmatic and metamorphic rocks, and associated mineralization (Kazmi and Jan 1997). Nearly 60% of the land area in the northern and western part of Pakistan is characterized by geologically complex mountain areas and incised highland topography while the remaining part is characterized by the alluvial plains of the Indus River system comprising its tributaries (Chap. 1, Fig. 1.3).

The Indus River basin (Chap. 1, Figs. 1.3 and 1.4) has a total area of 1.12 million km^2, distributed between Pakistan (47%), India (39%), China (8%), and Afghanistan (6%). Indus River originates from Tibet in China, runs the full stretch of the Khyber Pakhtunkhwa (KPK), Punjab, and Sindh provinces in Pakistan, and finally empties into the Arabian Sea (Ashraf et al. 1991). River Indus and its tributary rivers (Sutlej, Ravi, Chenab, and Jhelum) are the main sources of freshwater in Pakistan (Bhatti et al. 2017; Raza et al. 2016). The flow of the Indus decreases in winter and floods the banks during the monsoon season (FAO 2012).

The Indus basin irrigation system in Pakistan is the backbone of the country's economy. It includes 3 major multipurpose storage reservoirs, 19 barrages, 12 link canals, 45 major irrigation canal commands (covering over 18 million hectares), and more than 120,000 watercourses delivering water to farms and other productive uses. These canals operate concomitantly with a vast practice of groundwater extraction from private tube wells (Yu et al. 2013).

Indus basin is an extensive unconfined groundwater aquifer system, covering a gross command area of approx. 16 million ha (FAO 2012; Qureshi 2011). During the last decades, there has been a shift from surface water resources to groundwater resources within the Indus basin, mainly attributed to increase in population, availability of inexpensive drilling techniques, and adaptive behavior due to climate change.

24.3 Extent of Arsenic Contamination of Groundwater in Indus River Basin

The first case of groundwater As contamination in Pakistan was reported by Rahman et al. (1997). They analyzed groundwater samples from Karachi, the biggest city of Pakistan and a megacity in Asia, and reported As concentration of 80 μg/L. The authors attributed the contamination of the groundwater source to uncontrolled industrial discharge and open dumping of waste. The issue of As in groundwater gained more attention in 1999, while the Pakistan Council of Scientific and Industrial Research (PCSIR) and the Pakistan Council of Research in Water Resources (PCRWR) conducted a survey to determine the prevalence of As in groundwater (Azizullah et al. 2011; Haque 2005; Haque and Nasir 2015). The survey was preliminary and limited to only six districts in Punjab (Jhelum, Chakwal, Attock, Rawalpindi, Sargodha, and Gujarat). The survey reported that 14% of the 308 collected samples were contaminated with As concentration of >10 μg/L, the WHO guideline for As in drinking water (Haque 2005). Subsequently, a national survey was initiated in 2001 with a joint effort of UNICEF, LG&RD, PCRWR, and PCSIR. This time groundwater from 35 districts was analyzed, both in field and laboratory. It was found that the field kits underestimated

Table 24.1 Arsenic contamination in groundwater of the four provinces in Pakistan according to the National Survey of 2001 (Haque 2005)

	No. of samples		% of samples with As higher than WHO guideline	
Province	Field	Lab.	Field	Lab.
Baluchistan	619	71	1.3	1.4
KPK	1560	156	0.3	22.0
Punjab	4315	428	12.2	36.0
Sindh	2218	193	11.0	26.0
Total	8712	848	9.0	28.0

As concentration. Nevertheless, it was revealed that As contamination was prevalent in the two most populated provinces of Indus River basin in Pakistan, namely Punjab and Sindh (Haque 2005, Haque and Nasir 2015). The results by province are presented in Table 24.1.

Later on, more surveys were conducted by PCRWR, as part of the National Water Quality Monitoring Program (NWQMP) in various parts of the country (Azizullah et al. 2011; Farooqi 2015). It was confirmed that As in groundwater was widespread in major districts of Punjab (e.g., Multan, Sheikhupura, Lahore, Kasur, Gujranwala and Bahawalpur, Rawalpindi, Sargodha, and Sialkot) and Sindh (e.g., Hyderabad, Karachi, Sukkur) (Azizullah et al. 2011; Farooqi 2015). It was estimated that in Punjab over 20% of the population was exposed to As concentrations higher than the WHO guideline. In Sindh, even worse situation was reported, with 36% of population exposed to As concentrations higher than the WHO guideline (Ahmad et al. 2004). More cases of groundwater As contamination in Punjab and Sindh are discussed in the next sections.

24.3.1 Punjab

Nickson et al. (2005) were the first ones to study As contamination of groundwater in Punjab with the aim of elucidating the mobilization mechanism. Their study was based in Muzaffargarh District of Punjab which lies on the Thal Doab, between the Indus River and the Chenab River. It was proposed that the elevated As concentrations in the samples collected from the urban wells in Muzaffargarh were due to the reduction of iron oxides, triggered by the presence of high natural organic matter (NOM).

Arsenic contamination of groundwater in eastern Punjab has been reported (Farooqi et al. 2007a, b). In Kalalanwala and Kot Asadullah villages of Kasur District, 91% of the groundwater samples were contaminated with As, reaching up to 1900–2400 µg/L. The concentration of As was significantly higher at shallow depths, with predominance of As(V) as the aqueous species (Farooqi et al. 2007a, b). Masuda et al. (2010) studied the geochemical characteristics of aquifer sediments in the same study area, however, could not identify the main mechanism of As mobilization and proposed that the As contamination was either due to the anthropogenic sources, e.g., industrial waste, or from leaching of naturally occurring detrital chlorite (Masuda et al. 2010).

Several studies have focused on As contamination of groundwater sources in and around Lahore city. More than 7 million people live in Lahore and use groundwater for drinking and other household purposes. Taskeen et al. (2009) reported As concentrations higher than WHO guideline in the groundwater samples collected in old Kahna, a small town near Lahore. The As concentration in samples collected from Ravi River in Lahore was reported to be 2400 μg/L (Farooqi et al. 2009). The untreated industrial and sewage wastes arising from industries and metropolitan activities make their passage to the Ravi River. The water from Ravi River is used for irrigation where it could be the cause of soil contamination (Farooqi 2015). Akhter et al. (2010) reported groundwater As concentrations ranging between 24.6 and 71.6 μg/L in Lahore. Another study conducted by Akhtar et al. (2014) reported high As in the groundwater samples collected from adjacent areas of two dumping sites (Mehmood Booti landfill and Saggian landfill) in the vicinity of Lahore. Muhammad and Zhonghua (2014) also investigated the influence of a landfill site on groundwater quality near Lahore. Sixteen sampling points in the vicinity of the landfill for groundwater sampling were used. It was found that As concentrations were much higher than the WHO guideline in all the samples.

A recent study by Sultana et al. (2014) investigated the temporal variation in As concentration and the influence of abstraction depth in three selected villages in the proximity of Lahore (Manga Mandi, Shamki Bhattian, and Kalalanwala). Thirty groundwater samples were collected, 20 from shallow hand pumps installed at 24–36 m, 9 samples from 40 to 80 m, and 1 sample from a deep tube well 80–200 m in depth. Arsenic concentration in the water samples varied considerably ranging from 1 to 525 μg/L. 84% samples showed As levels higher than the WHO guideline. Elevated As concentrations were noticed compared to 2007 (Farooqi et al. 2007a). The highest concentrations of As were found to be present in the shallow aquifers. Therefore, the authors proposed that the increase in As concentration was due to increased fertilizer use between the two sampling campaigns. Abbas et al. (2015) studied the quality of drinking water from the source wells and distribution system in Lahore. A total of 50 groundwater samples were collected from various urban settlements in Lahore (Shahdara, Mughalpura, Gulberg, Misri Shah, Shad Bagh, Ichhra, Basti Saden Shah, University of Engineering and Technology, Queens Road, Ali park, Gunj bakhsh town, Quaid-e-Azam Estate (Township), and Bank Square (Old Anarkali)). All the samples showed As concentrations higher than the WHO guideline and concentrations ranged between 13.4 and 82.8 μg/L.

In a recent study, Abbas et al. (2016) investigated the spatial variability of groundwater chemistry in seven towns within Lahore city focusing on the distribution of As (and fluoride). Based on the investigations on 472 well water samples, the study indicated significant variations in the distribution of As, total dissolved solids (TDS), alkalinity (HCO_3) and NO_3 in groundwater. In general, As concentrations were found to be considerably high in the northeastern part of the city which was attributed to the heterogeneity of the aquifers as well as major industrial activities. Major ion chemistry of the groundwater samples indicated considerable variations with predominance of Ca–Mg–HCO_3–SO_4 water type together with a range of other Mg–Ca–HCO_3–SO_4, Ca–Mg–HCO_3–SO_4–Cl, Ca–HCO_3–SO_4, and Ca–Mg–SO_4–HCO_3 water types which indicate that both carbonate weathering and probable silicate weathering control the major ion chemistry of the groundwater. Results of hierarchical cluster analysis revealed that the distribution and mobilization of As in groundwater were predominantly controlled by pH. Thus, the groundwater chemistry is primarily controlled by mineral dissolution and precipitation reaction during the water–solid phase interactions in the aquifers and the elevated concentration of As controlled by pH under the oxic conditions in the aquifers.

Malana and Khosa (2011) studied randomly collected groundwater samples in Dera Ghazi Khan District of Punjab. 22% of the 32 collected samples contained high As concentrations. The mechanism of As mobilization could not be elucidated; however, based on the data, it was proposed that the mobilization might be due to the reduction of iron oxides in the presence of natural organic matter (NOM).

Shakoor et al. (2015) studied the groundwater samples from three previously unexplored rural areas in Punjab (Chichawatni, Vehari, Rahim Yar Khan). Total 62 samples were collected. It was found that 53% of the groundwater samples had higher As concentration than the WHO guideline, ranging between 1.5 and 201 μg/L. Moreover, As(V) was the dominant specie of As, though As(III) was also present. Rafique et al. (2014) aimed to assess the quality of drinking water in Jampur Tehsil located in Rajanpur District in South Punjab. Based on the analysis of the samples collected from different sources, e.g., as hand pump, injector pump, tube well, and water supply line, it was reported that majority of the population was exposed to elevated levels of As.

24.3.2 Sindh

In Sindh, Manchar Lake and groundwater in the vicinity have been under focus of many studies. Manchar is the largest freshwater lake in Pakistan, situated in Dadu District. Its water is used for agriculture, fishing, drinking, and general household use (Farooqi 2015). Arain et al. (2008) studied As in Manchar Lake in summer and winter seasons and reported As concentrations that were 6–8 times higher than the WHO guideline for As in drinking water. In summer, As concentrations ranged from 60.4 to 88.9 μg/L, and in winter, they ranged from 64.9 to 101.8 μg/L. Another study by Arain et al. (2009) showed that water in Manchar Lake contained As concentrations in the range of 35–157 μg/L. Moreover, the groundwater samples collected from the adjacent areas of the lake showed As concentrations that were significantly higher than the WHO guideline, in the range of 23.3–96.3 μg/L. Arain et al. (2009) also revealed that the vegetables and selected crops accumulated higher As compared to food commodities collected from unaffected areas. Kazi et al. (2009) evaluated the impact of As toxicity on health of local population around Manchar Lake by studying the biological samples (scalp hair and blood). Strong correlations were observed between As concentrations in drinking water versus hair and blood samples of exposed skin disease (Kazi et al. 2009). Arain et al. (2007) analyzed the groundwater samples from different depths in districts Matiari and Khairpur Mirs. Approximately 40% of the samples indicated As concentration of ≥ 50 µg/L and 15% of the samples indicated As concentration of >250 µg/L.

Khan et al. (2008) reported that As concentrations in the groundwater samples collected in Hyderabad city were in the range of 25–1286 µg/L. A study at Jamshoro District of Sindh reported As concentrations ranging between 13 and 106 µg/L in groundwater (Baig et al. 2009). The authors concluded that the elevated As in the groundwater was due to widespread waterlogging from Indus River irrigation system that caused high saturation of salts and led to enrichment of As in shallow groundwater (Baig et al. 2009). Baig et al. (2011a) studied the uptake of As by grain crops grown on agricultural soils in three sub districts of Khairpur (Faiz Ganj, Thari Mirwah and Gambat), irrigated by tube well water and canal water. The tube well water contained much higher average As concentration (15.4 ± 2.31 µg/L at Faiz Ganj, 31 ± 8.21 µg/L at Thari Mirwah and 98.5 ± 68.7 µg/L at Gambat) than the canal water. Baig et al. (2011a) reported that a significantly high accumulation of As was taken place in grains grown on tube well water compared to those grown on canal water. The authors proposed anthropogenic activities (agricultural, industrial, domestic) for the increased concentration of As in tube well water.

The As contamination of drinking water in Thar Desert has been under focus of many studies. Tharparkar District is an extreme arid area, freshwater is scarce, and (deep) groundwater is saline. Rashid et al. (2012) carried out a study in which they collected 99 water samples from 33 different locations in Tharparkar District. Groundwater samples of two villages, namely Murid Khan Umarani and Khan Khanjar Reham, were found contaminated with As concentrations of higher than the WHO guideline. Brahman et al. (2013a) studied the groundwater contamination by As and its species in Diplo and Chachro subdistricts in Tharparkar. All groundwater samples were collected directly from the wells that were >12 m deep. The concentrations of As were 10–250 times higher than the WHO guideline. In Chachro, As concentrations up to 1390–2480 µg/L were reported, and in Diplo, 112–840 µg/L As concentrations were reported. Although As(V) was reported to be the dominant specie in water, As(III) was also present in significant concentration. The authors proposed that pyrite oxidation and evaporative concentration of As in shallow aquifer were the mechanisms involved in As mobilization. Brahman et al. (2014) reported As concentrations in the range of 360–683 µg/L in the samples collected from surface water ponds in Nagarparkar, a subdistrict in Tharparkar. In another study, Brahman et al. (2013b) investigated As and (F^-) contamination of groundwater in Mithi and Nagarparkar subdistricts of Tharparkar. Groundwater samples were collected from 14 different villages (Bhalwa, Danodandhal, Veraval, Nagarparkar, Islamkot, Moryotar, Sakrio, Pabuar, Mithi, Jeeando Daras, Budhe Jo

Tar, Mthrao, Lunyo, and Haday Jo Tar). Arsenic concentrations ranging from 100 to 3830 μg/L were reported, and As(V) was found to be the dominant specie of As. Arsenic showed positive correlation with all studied physicochemical parameters except NO_3^-, CO_3^{2-} and pH.

24.4 Conclusion and Future Outlook

In groundwater across Punjab and Sindh provinces, that constitute an extensive part of Indus River basin, As concentrations significantly higher than the WHO guideline have been reported in a number of research studies as well as national surveys. Both natural and anthropogenic processes have been primarily indicated as cause for elevated As concentration in groundwater. An increasing number of studies also show evidence that irrigation with As contaminated groundwater is associated with elevated As concentration in agricultural products.

The future research should therefore focus on the detailed understanding of the complexities of the geological setting of Pakistan to outline the sources of As from different geotectonic domains and the metallogenic provinces and their transport to the Indus basin across the provinces of Punjab and Sindh. Moreover, detailed hydrogeological studies are also imminent to unravel the mechanistic understanding of the mechanisms of As mobilization in groundwater in different parts of the Indus basin.

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