

# A comprehensive review on current status, mechanism, and possible sources of arsenic contamination in groundwater: a global perspective with prominence of Pakistan scenario

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**Abstract** Arsenic(As)-mediated contamination of groundwater resources in different parts of the world is a consequence of natural or anthropogenic sources, leading to adverse effects on the environment and human health. Millions of people from different countries are unfortunately consuming groundwater contaminated with alarming levels of As. Exposure to the high concentration of As for an extended period of time can cause devastating effects on human health such as skin lesions, cardiac disorders, discolouration and cancer. Until 2018, about 11 districts of Sindh and Punjab provinces in Pakistan had been found with As contamination in groundwater beyond the national defined permissible level, i.e. 50 µg/L. Tharparkar and

Hyderabad (in Sindh province) along Indus river and Lahore and Kasur (in Punjab province) are well-known hotspots sites of natural geogenic As contamination in groundwater. Higher levels of Sulfates ( $\text{SO}_4^{2-}$ ), Chloride ( $\text{Cl}^-$ ) and Carbonate ( $\text{CO}_3^{2-}$ ) along with the elevated values of electrical conductivity and basic pH, as well as augmented presence of “As V” species, were all an indication of oxidizing condition in groundwater, and these oxidizing conditions are identified as the primary mechanism of As contamination into aquifers of Pakistan via oxidative dissolution. The main aim of this review is to summarize and discuss the current contamination status of As in groundwater water globally with a special focus on Pakistan scenario, isotopic evidence to track sources of groundwater recharge and its effects on As contamination in groundwater with various redox conditions prevailing in Pakistan. In addition, public health consequences of As contamination and mitigation strategies for As removal from water resources have been also highlighted. In this review, the data were extracted from various cutting edge studies published in national and international journals.

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## Introduction

Arsenic(As), a trace element that is well known for its toxic and ubiquitous nature. The United States Environmental Protection Agency (USEPA) and World Health Organization (WHO) devised the permissible limit value of As in groundwater as 10 µg/L (Hassan et al. 2009). However, the permissible limits of As also set to 50 µg/L in many of the developing countries (Nickson et al. 2005). The mobility, toxicity, and fate of As in different environmental matrices determined by multifaceted series of control dependent on biological process, chemical speciation and mineralogy of the area (Bowell et al. 2014). Contamination of groundwater through As is among the most critical and serious environmental problem, especially in the developing countries due both to the high toxicity of As and its ability to induce deleterious health effects even at a low exposure levels (Mandal and Suzuki 2002). As and other metalloids mobility and accumulation in water depend on physicochemical conditions and nature of the water (Gao and Li 2012). As contaminates both surface and groundwater as well as enters into the food chain like foodstuff and vegetables (Muhammad et al. 2010), and chronic exposure to As through contaminated water and food causes severe health problems such as melanosis, hyperkeratosis, and hypertension, cardiovascular disease (Thundiyl et al. 2007) skin lesions, anemia, lung diseases and peripheral vascular diseases (Mandal and Suzuki 2002). Globally, the natural contamination of As has been reported in drinking water supplies in more than 70 countries and the majority of these nations belong to South Asian and Southeast Asian regions (Raven-scroft et al. 2009). The elevated levels of As > 50 µg/L in water have been reported in different countries of the world like Argentina, Bangladesh, China, Chile, Hungary, India, Pakistan, Mexico, Vietnam and as well as in many parts of the USA (Smedley and Kinniburgh 2002). The presence of As in environment has gained considerable attention in the last decade because studies have reported alarming contamination levels of As in West Bengal of India and neighboring locations in Bangladesh (Nickson et al. 2000; Das et al. 2004). Similar to the other developing nations, Pakistan is also facing serious issues of water shortage and contamination in the available water resources. Previous reports showed that Pakistan has mostly exhausted its available freshwater resources due to

low water storage capacity (Azizullah et al. 2011). Now the country included in water stressed nations and if this scenario continues, it will likely to declare as water scarce nation (Hashmi et al. 2009) (Pakistan 2007). Worldwide, approximately 1.1 billion people have no access to clean water for drinking, about 2.5 billion people have lack of proper sanitation facilities, and waterborne disease-mediated annual death toll has been exceeded more than 5 million (Hinrichsen and Tacio 2002). According to national survey, only 56% households in Pakistan have access to clean and safe drinking water (Farooq et al. 2008; Ullah et al. 2009). This situation is more worse in the eye of the international standards for safe and drinkable water, because as per international standards only 25.61% people in Pakistan have access to safe drinking water and this population includes 23.5% rural and 30% urban masses (Rosemann 2005). Anthropogenic activities are mainly responsible for contamination of drinking water in densely populated areas of Pakistan, and authorities have declared groundwater as not drinkable in cities such as Gujarat, Sialkot, Kasur, Faisalabad, Peshawar, Rawalpindi, Lahore, and Karachi (Bhutta et al. 2005). Similar situation is also prevailing in the capital of Pakistan and its twin city Rawalpindi, where water samples were reported to contaminate with the total coliforms and fecal coliforms, respectively at the percentages of 94 and 34% (Jehangir 2002). Therefore, most of the people are consuming commercially available bottled water for drinking, which is an expensive option and not affordable for a large proportion of population. However, this so-called mineral water is also not completely safe due to the sub-standard water purification plants and lack of their proper monitoring process (Rosemann 2005). Consequently, a significant number of households in Pakistan are exposed to contaminated water that is resulted in the increase in incidences of waterborne diseases and other health effects. Therefore, the main aim of this review is to highlight possible causes of As contamination in groundwater, associated health risks, and the best available strategies to mitigate As pollution in groundwater. This review will further assist in implementation of cost-effective, efficient, and suitable mitigation strategies for safe water provision to the rural and remote areas in the developing countries. To serve this purpose, knowledge of the groundwater quality and the recharge rate is essential. The environmental

isotopic analysis-based techniques have emerged as widely and commonly used approach during the last decades to understand the full spectrum of the status of water resources, its development and management. Therefore, the application of these new techniques has made it easier to understand the hydrological problems and find their appropriate solutions.

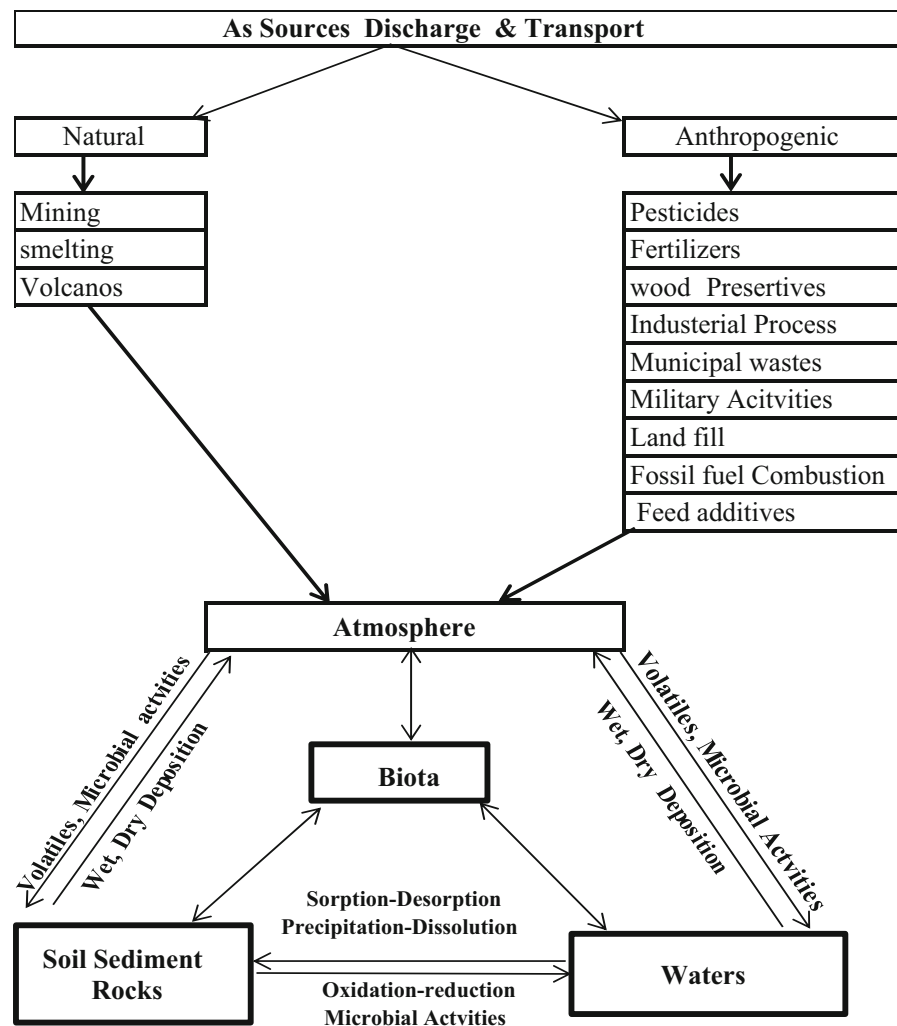
### Environmental fate and sources of Arsenic

As is the twentieth most abundant element in earth crust and a well-known human carcinogen metalloid with atomic number 33, and it has only one isotope that exists in nature with atomic mass 75. As has four oxidation states ( $-3$ ,  $0$ ,  $+3$  and  $+5$ ) (Mandal and Suzuki 2002; Smedley and Kinniburgh 2002). Anthropogenic or non-natural sources of As arise from the human activities such as mining, smelting, metal ores processing (tin, gold, copper and also zinc) that cause the release of As into the environment (Barringer and Reilly 2013). The ancient and recent smelting process that also cause the release of As into environmental compartments (Fig. 1) such as air and soil at locally and globally (Matschullat 2000). As compounds are widely used in manufacturing industries, wood-preservation and also in glass production units (Welch et al. 2000a). In the past, As and As compounds are widely used for the preparation of insecticides, pesticides and herbicides, fungicides and also used as feed additives (Compendium 1975; Mandal and Suzuki 2002). The anthropogenic sources of As also include municipal, industrial and domestic waste disposal into the water system, and coal combustion is also another source of As pollution in different environmental matrices (Rahman et al. 1997; Farooqi et al. 2007b; Arain et al. 2009a; Baig et al. 2009; Shah et al. 2009). As exists in nature in over 200 various form of minerals, of which around 60% are arsenates, 20% sulfides and sulfosalts and leftover 20% are oxides, arsenide, arsenates, silicates and As in elemental form (Mandal and Suzuki 2002) of which only a few of these are commonly contain significant amounts of As (Table S1) (Gomez-Caminero et al. 2001). There are four natural geological processes responsible for the release of As to the various environmental compartments, which include alkaline desorption, sulfide oxidation, reductive dissolution, and other geothermal activities (Brammer and

Ravenscroft 2009). Regarding South Asian region, the process of reductive dissolution is the most critical mechanisms that causes release of As into environment. As usually adsorbed on the surface of iron oxyhydroxides in the sediments and as a result of microbial degradation, it enters into the environment. When the organic matter undergoes microbial degradation, the ferric iron reduces to the soluble form, i.e. ferrous and As releases into the groundwater system (Nickson et al. 2000). The natural sources of As also include the desorption of FeOOH and oxidation of As-bearing sulfide minerals (Farooqi et al. 2007b). As also derives from other natural sources, presumably from the detrital chlorite (Masuda et al. 2010).

### Geochemistry of Arsenic

As mainly exists in two main forms, organic As and inorganic As and have four oxidation states and all of these are present in the environment. Depending on the environmental conditions, As frequently present in the form of sulfides, metal arsenide or arsenates (Smedley and Kinniburgh 2002). In surfacewater, As present in organic form, while groundwater usually contain its inorganic form, which is much more toxic than organic forms of As. The reduced form of As in groundwater present as oxyanions of arsenite As(III) and or oxidized form of arsenate As(V) (Smedley and Kinniburgh 2002). pH and oxidation–reduction potential (Eh) are two most important factors that control speciation of As and its solubility into the groundwater (Mandal and Suzuki 2002; Gupta and Gupta 2013). At neutral and faintly acidic pH, As(III) is present as non-dissociated salts, while at  $\text{pH} > 8$  a significant number of anionic species of As were found. As(V) is completely broken down and exists in the form of monovalent, divalent, and trivalent As anions in the aquatic environment (Bard et al. 1985). In surface water and oxygenated water under oxidizing conditions, As(V) species, e.g.,  $\text{H}_3\text{AsO}_4$ ,  $\text{H}_2\text{AsO}_4^-$ ,  $\text{HAsO}_4^{2-}$  and  $\text{AsO}_4^{3-}$  are dominant and stable. Under reducing conditions, the arsenious acid is abundant and mostly available as neutral  $\text{H}_3\text{AsO}_3$  (Cullen and Reimer 1989). The reduction of As(V) to As(III) takes place due to the bacterial action or chemical reduction. The reduction process is relatively prolonged and not the complete conversion of As(V) to As(III), that is

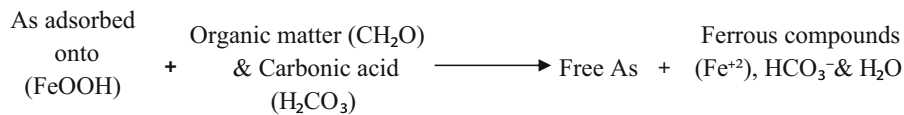


**Fig. 1** Sources of Arsenic, Fate, and Transportation between Environmental Compartments

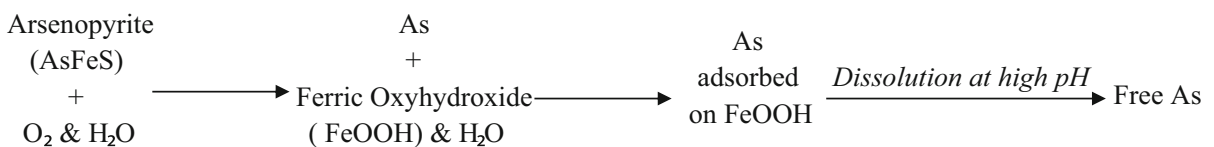
why both forms of As species exist in anoxic groundwater and present in oxic or surface water (TRC, 2005). The evaluation of oxidation/reduction (redox) conditions in the groundwater is often a prerequisite for understanding the behavior of the contaminants in aquifer system, while certain undesirable by-products generated because of redox processes and redox-sensitive elements (Table S2). These primary redox-sensitive species mostly dissolved ions such as Fe(II), methane and sulfates, nitrates and their presence reflects redox conditions. Evaluation of these ions is relatively cost-effective and easier, and they are routinely measured in regional water quality assessments (Christensen et al. 2000). Generally, the two main hypothesis

are accepted to understand As mobilization mechanisms within environmental compartments, the first is desorption of As under reducing conditions from iron-rich hydro-oxide minerals (Korte 1991; Nickson et al. 1998; Nimick 1998; Chadha and Ray 1999; Chowdhury et al. 1999), and the second is the oxidation of As-rich sulfide minerals (Mandal 1996; Smedley et al. 1996; Farooqi et al. 2007a). These processes of As mobilization enhanced by the various bacteriological and chemical reactions such as adsorption, perceptions, volatilization and methylation, which ultimately increased the mobility and availability of As in environment (Gupta and Gupta 2013). Under reducing conditions, the dissolution of As-bearing iron oxides is the primary source of As

contamination in groundwater sources of South East Asian countries (Nickson et al. 2000; Smedley and Kinniburgh 2002; Kim et al. 2011). The process of reductive dissolution of iron-oxide is well known in anoxic groundwater having (pH ~ 7) low level of dissolved oxygen with biological degradation of organic matter that ultimately reduced the ferric ions to soluble ferrous form (Nickson et al. 2000; Ravenscroft et al. 2009). The aquifers that contain low concentration of sulfates (SO<sub>4</sub><sup>2-</sup>) and nitrates (NO<sub>3</sub><sup>-</sup>) anions and a higher concentration of iron (Fe) and manganese (Mn) that specify the aquifers conditions undergoing reductive dissolution of iron oxides process is prevailing (Stüben et al. 2003). The South East Asian countries such as Bangladesh, India, China, and Vietnam are mostly affected by this process. However, worldwide 64% of As contamination in groundwater is due to this process (Ravenscroft et al. 2009). The equation for reductive dissolution of iron-oxide process is given below (Zheng et al. 2004).



The process of mineralization takes place within sulfide-rich regions, frequently associated with the rare metals such as Gold and Tin. The mining activities of such kind of minerals lead to cause oxidation of As-bearing minerals mainly arsenopyrite and pyrite cause As contamination in groundwater (Smedley and Kinniburgh 2002). The aquifers prevailing in mining regions contain elevated level of SO<sub>4</sub><sup>2-</sup>, dissolved oxygen (DO) and pH < 7 (Smedley et al. 1996; Smedley and Kinniburgh 2002). The various regions of different countries facing exaggerated mining related release of As in groundwater including USA, Thailand, Mexico, Greece, Colombia and Ghana are profoundly affected by this process. The oxidation of sulfide minerals (pyrite oxidation) equation (Zheng et al. 2004).



### Health impacts of Arsenic

As is one of the most toxic and cancer-causing metalloids in context of human health throughout the world. The daily intake of As-contaminated drinking water cause acute and chronic health effects. As contamination in groundwater has been reported as a threat to human health in different countries such as Pakistan, India, Bangladesh, China, Vietnam, Argentina, Cambodia, USA and Nepal (Haque et al. 2007; Nguyen et al. 2009; Muhammad et al. 2010; Phan et al. 2010; Azizullah et al. 2011; McClintock et al. 2012; Navoni et al. 2014; Tsuji et al. 2014). The daily intake of As-contaminated water through drinking water causes decrease in the generation of white and red blood cells and also induces damage to the blood vessels to create “pins and needles” types of sensation in the hands and feet of the exposed individual (Abernathy et al. 2003). The chronic exposure of As damage human cardiovascular system, dermal, pulmonary system, neurological system, hepatic, respi-

ratory system and reproductive system (US Department of Health and Human Services 2000). As shown in Table S3 (Barringer and Reilly 2013), about 80–100% ingested and inhaled As observed in lungs and gastrointestinal tract (Shemirani et al. 2005). The alarming levels of As in the drinking water as high as 300 µg/L can increase the risk of incidences of heart diseases (Wade et al. 2009) about 98.65% population of Cambodia were highly vulnerable toward non-cancer health effects by the daily intake of As-contaminated water and 33.7% population threatened toward cancer (Phan et al. 2010). A comprehensive study (Wade et al. 2009) conducted in Mongolia that reported as approximately 12,600 peoples were at the risk of heart disease due to the elevated As concentration in groundwater, i.e., 300 µg/L. Further, about

98.6% population in Cambodia is also at the risk of non-cancer health effects and among them about 33.7% highly prone for induction of cancer due to the consumption of As-contaminated water (Phan et al. 2010). In Bangladesh, the consumption of As-laden water resulted in hyperpigmentation and hyperkeratosis among the people, which are most common symptoms of diseases that can lead toward cancer (Nguyen et al. 2009). Further, (Kazi et al. 2009) conducted a study in Pakistan that revealed around 61–73% residents around Manchar Lake were suffering from As mediated chronic toxicity cases in terms of keratosis and melanosis. Another study conducted in Bobak village, which is in the vicinity of Manchar Lake, where the cases of rough skin diseases and skin lesion were reported in 30–40% residents (Arain et al. 2009b).

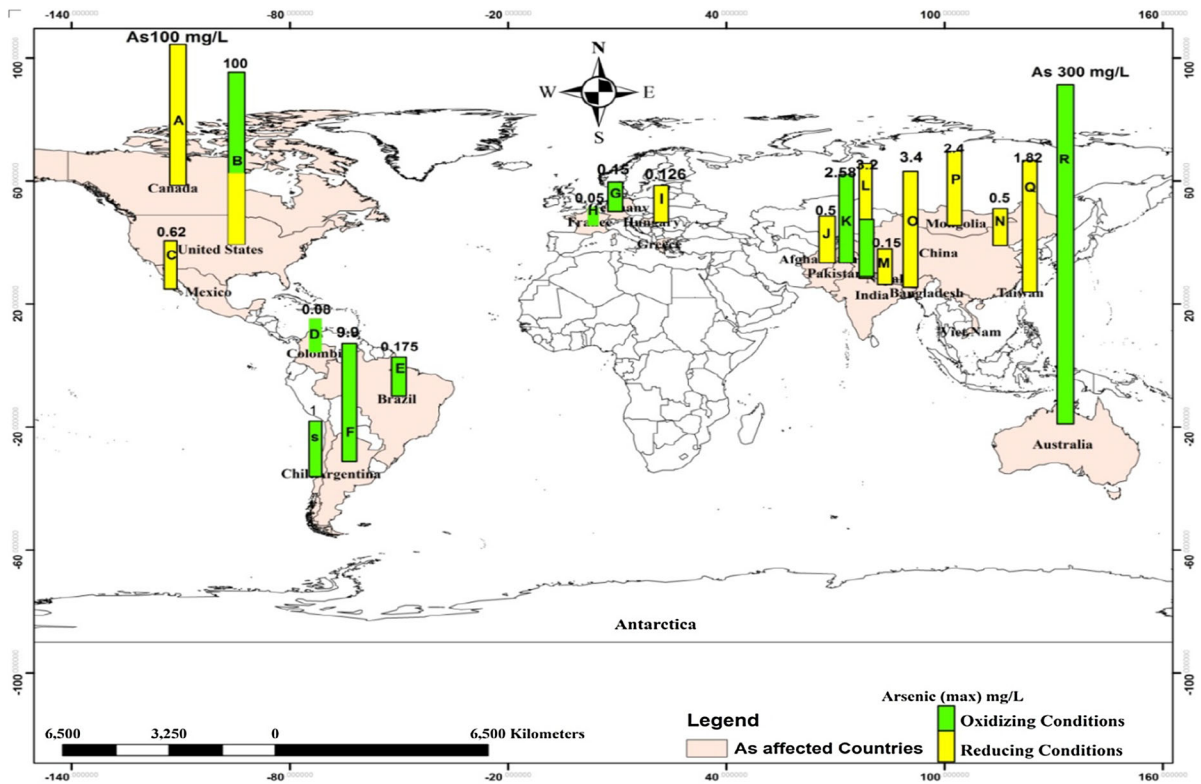
### Worldwide Arsenic contamination in groundwater

As contamination in groundwater is one of the primary concerns last two decades across the globe. Various studies of diverse aquifers in the different parts of the world showed the concentration of As above 50 µg/L that can certainly cause significant health problems. The most As-contaminated countries of the world are Argentina, Hungary, Mexico and different parts of the USA. The South East Asian countries such as India, Bangladesh, China, Nepal and Vietnam are also at alarming risk of As contamination (Mandal and Suzuki 2002; Smedley and Kinniburgh 2002; Agusa et al. 2004; Stanger et al. 2005; Mukherjee et al. 2006; Yadav et al. 2014). According to Kim et al. 2002, the maximum concentration of As in Canada about 100 mg/L reported in groundwater, the thermal springs and mining activities are significant sources of As release into groundwater under oxidizing conditions. The most As-contaminated country of the world is Australia, where the concentration of As was reported up to 300 mg/L, and mining activities, oxidation of sulfide-bearing minerals and volcanic eruptions were observed as the significant sources of As release in groundwater (Boyle et al. 1998). India and USA have mixed environmental factors, reducing and oxidizing conditions, which are also prevailing in different countries worldwide that affected As contamination in groundwater (Fig. 2). Further, the geological and ecological processes and factors also

control As contamination in groundwater as details mentioned in (Table 1).

### Status of Arsenic contamination in Pakistan

According to geographical characteristics, the Indus Plain is situated in the east of Pakistan; the three gigantic mountain ranges such as the Karakoram, Himalaya, and Hindu Kush are located in the north; and the other mountain regions in the northwest; and lastly, the Balochistan plateau is located in the west. Except for the temperate northwest and climate of the region is arid to semiarid. The different areas of the Pakistan (Sindh and Punjab Provinces) cover under the Indus River, which is the main river in the country with estimated length of 3180 km. The most important aquifers of Pakistan are situated in Indus Plain, and this area is consisted of permeable soils with low organic content and exhibited up to 300 m of quaternary sedimentary deposits (Greenman et al. 1967). Further, the groundwater yields range in Indus Plain is ranged between 100 and 300 m<sup>3</sup>/h at 150 (m) depth. While the neighboring desert regions are usually predominated with sands dunes. The availability of groundwater in desert area is from 10 to 50 m<sup>3</sup>/h. Moreover, the permeable gravels are also found up to some extent in the northwest region (Smedley 2001). Indus Plain of Pakistan holds a population over 100 million and a significant proportion this population engaged in agricultural activities, and there is huge agriculture productivity in this area, due both to fertile soils and abundant water resources (Fig. 3). A significantly large number of people reside along the river banks in the big cities and small towns. There are nearly 27 districts in this Indus region with 40 million residents, whereas the Indus River is, moreover, flowing through big cities, and population are living alongside the river (Rabbani et al. 2017). Because of arid climate in the region, widespread irrigation system is consisted of extensive canals and small waterways widely uses the river Indus to its key branches crossways on the adjacent plains and also extracted through tubewells. The Indus plain and predominantly quaternary sediments mainly consist of alluvial and deltaic origin and thickness of sediments from meters to several hundred meters in various parts of the country. The aquifers present these sedimentary areas highly contaminated with the As concentrations.



**Fig. 2** Status of As (mg/L) contamination in groundwater all over the world (A) Kim et al. (2002), (B) Robertson (1989), Welch et al. (2000a, b), Smedley and Kinniburgh (2002), (C) Carrizales et al. (2006), (D), Boyle et al. (1998), (E) Matschullat et al. (2000), (F) Hopenhayn-Rich et al. (1996), Smedley and Kinniburgh (2002), Hudson-Edwards and Archer (2012), (G) Wolf (1974), (H) Cadic (2002), (I) Aposhian et al. (2000), Rowland et al. (2011), (J) Saltori

(2004), (K) Nickson et al. (2005), Farooqi et al. (2007a), Arain et al. (2009a), Muhammad et al. (2010), (L) Kinniburgh et al. (2000), Nickson et al. (2000), Smedley (2005), Mukherjee and Fryar (2008), (M) Gurung et al. (2005), Thakur et al. (2010), (N) Kinniburgh (2001), Xie et al. (2008), (O) Zheng et al. (2004), Halim et al. (2009), (P) Ma et al. (1999), Smedley (2005), (Q) Liu et al. (2003), (R) Boyle et al. (1998) and (S) Sancha and Castro de Esparza (2000)

Due to the arid climate and presence of ancient Pleistocene deposits, unconfined and aerobic conditions of aquifers make the less mobilization of As (Smedley 2005). The recent deposits of alluvial and deltaic sediments especially in Pakistan (Sindh and Punjab regions), India (West Bengal regions) and Bangladesh have been very similar type geochemical nature; it is predicted that the processes of As mobilization are almost same. In Pakistan due to the oxidizing conditions and the presence of unconfined aquifers that cause the much lower concentration of As in groundwater as compared with India and Bangladesh (Cook 1987). The different studies show the several areas of Sindh and Punjab provinces are highly affected with As by both anthropogenic as well as natural sources of As in groundwater defined by (Nickson et al. 2005; Farooqi et al. 2007a). The

population along the Indus River exposed to higher levels of As > 10 µg/L in terms of drinking ground water; and approximately 13 million people out of total 40 million in 27 districts were more prone to As-contaminated drinking water. However, the estimated total population of Pakistan was 182 million in 2013 (Rabbani et al. 2017). Moreover, the National As Survey revealed a total of 9% of water sources in Pakistan were observed with elevated level of As > 10 µg/L. Lately, a study was conducted by Rabbani et al. 2017 in district Khairpur (mirs) Sindh and found extremely high concentrations of As in 2517 groundwater water samples. The mean As concentration was reported at 14.98 µg/L, and maximum As level was observed at 350 µg/L. The mean distribution of As in Talukas is given in (Table 2). As shown in (Fig. 3), the Talukas (located near the River Indus) Sobo Dero,

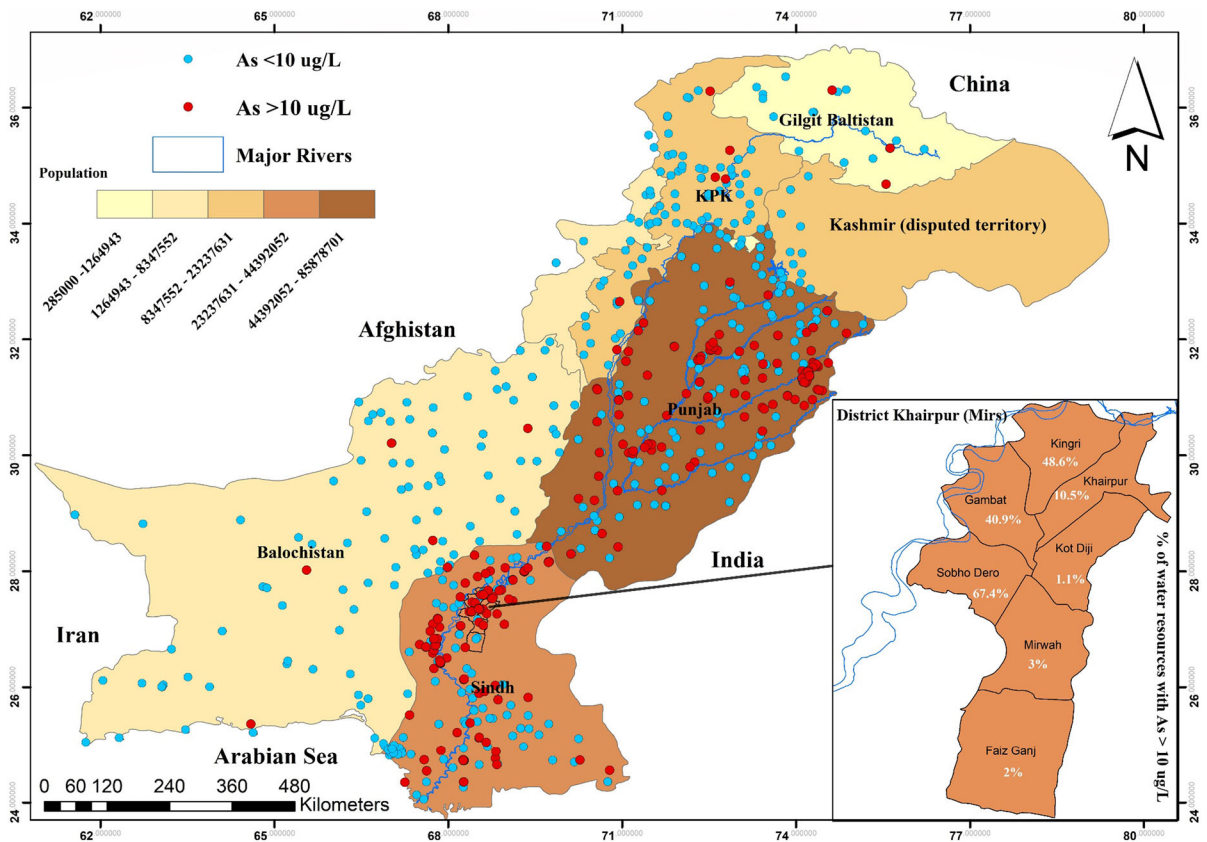
**Table 1** Worldwide As contamination in groundwater with environmental factors controlling As contamination and geological process

Country name	Process controlling As contamination in groundwater	Environmental factors and mechanisms	As concentration ( $\mu\text{g/L}$ ) ranges (min–max)	References
Afghanistan	Reductive dissolution	Reducing conditions and high content of organic matter	10–500	Saltori (2004)
Bangladesh	Reductive dissolution	Low level of $\text{SO}_4^{2-}$ , $\text{NO}_3^-$ and high content of organic matter, $\text{S}^{-2}$ , $\text{NH}_4$ , Fe and Mn	< 1–2500	Zheng et al. (2004), Halim et al. (2009)
China	Alluvial plains	Neutral pH, High content of organic matter and extreme reducing conditions	> 500	Kinniburgh (2001), Xie et al. (2008)
Nepal	Reductive dissolution	Neutral pH and reducing conditions	5–150	Gurung et al. (2005), Thakur et al. (2010)
China/ Taiwan Province	Black shale sediments	The high content of organic matter and very strong reducing conditions	5–1820	Liu et al. (2003)
Inner Mongolia	Holocene alluvial sediments	pH neutral reducing conditions	<1–2400	Ma et al. (1999), Smedley (2005)
Vietnam	Alluvial plains	Neutral pH and reducing conditions	5–3050	Berg et al. (2001), Berg et al. (2007)
Hungary	Alluvial plains	Reducing conditions	< 2–126	(Aposhian et al. 2000; Rowland et al. 2011)
India	Reductive dissolution, oxidation of arsenic-bearing sulfide minerals and alluvial sediments	Both reducing and oxidizing conditions	< 1–3200	Kinniburgh et al. (2000), Nickson et al. (2000), Smedley (2005), Mukherjee and Fryar (2008)
U.S.A	Evaporates presence and alluvial sediments	Both reducing and oxidizing conditions	> 100,000	(Robertson (1989), Welch et al. 2000a, b, Smedley and Kinniburgh (2002)
Argentina	Oxidizing conditions, desorption at high pH and thermal springs	High pH, Eh, $\text{SO}_4^{2-}$ , $\text{NO}_3^-$ and oxidizing conditions	< 1 to 9900	Hopenhayn-Rich et al. (1996), Smedley et al. (2002), Hudson-Edwards and Archer (2012)
Brazil	Gold Mining	pH neutral to acidic and high $\text{SO}_4^{2-}$	1–175	Matschullat et al. (2000)
Australia	Mining activities oxidation of sulfide-bearing minerals and volcanic eruption	pH neutral to acidic and high $\text{SO}_4^{2-}$	1–300,000	Boyle et al. (1998)
Canada	Thermal spring and mining activities	pH neutral to alkaline	< 1 to > 100,000	Kim et al. (2002)
Chile	Thermal spring and alluvial bedrocks	High salinity and oxidizing conditions	100–1000	Sancha and Castro de Esparza (2000)
France	Mineralization and gold mining	pH neutral to acidic and high $\text{SO}_4^{2-}$	10–50	Cadic (2002)
Germany	Ore mining activities	pH neutral to acidic	< 10–150	Wolf (1974)



**Table 1** continued

Country name	Process controlling As contamination in groundwater	Environmental factors and mechanisms	As concentration ( $\mu\text{g/L}$ ) ranges (min–max)	References
Pakistan	At high pH desorption, alluvial sediments and evaporative concentration	Arid environment, pH high, oxidizing condition and high $\text{SO}_4^{2-}$	< 1–2580	Nickson et al. (2005, Farooqi et al. (2007a), Arain et al. (2009a), Muhammad et al. (2010)
Mexico	Volcanic sediments	pH neutral and oxidizing conditions	4–620	Carrizales et al. (2006)
Columbia	Mining activities and presence of sulfide-bearing minerals veins in volcanic rocks	pH neutral	< 10–80	Boyle et al. (1998)



**Fig. 3** Spatial distribution of As contamination in groundwater of Pakistan

Kingri and Gambat were exhibited 67.4, 48.6 and 40.9% proportions of wells with  $\text{As} > 10 \mu\text{g/L}$ . The Khairpur district population is residing along Indus River at high risk of developing human health effects from long-time As exposure (Rabbani et al. 2017).

Recently, a study conducted by Podgorski et al. 2017 used new data collected from 1184 groundwater samples throughout Pakistan and estimated human health risk hazard of contaminated groundwater with As at threshold levels of 10 and  $50 \mu\text{g/L}$ . The

As > 200 µg/L were reported mainly in the southern partial side of the Indus plain, while As > 10 µg/L mainly measured along River Indus and its branches (Fig. 3). According to output of human health hazard model, the significant portion of Indus Plain is probable to exhibit the elevated As concentrations; however, the rest part of the country is mostly in the safe zone. Contrary to the other As-contaminated regions in Asia, the principal contributing factors in the release of As in Indus plain includes the extensive irrigation from unconfined aquifers and elevated pH dissolution resulting from basic topsoil. Moreover, pockets of reductive dissolution, human and animal organic waste, and intensive agricultural activities are also causing the release of As into the environment. Podgorski et al. 2017 estimated that around 50 to 60 million individuals that are using groundwater in this area are at the risk of diseases induction, with the hot spot locations around Hyderabad and Lahore. Though (Niazi 2017) response against (Podgorski et al. 2017) and suggest a total of 1184 groundwater samples were taken in this study, of which 399 wells were below the WHO safe limit of As and 785 were found above this limit. It is now clear from various blanket surveys that distribution of As varies widely, both vertically and spatially and cannot be accurately predicted by sporadic testing of water from a small number of wells. In this study, randomly only 1184 samples have been taken, and authors have predicted from results of 785 samples exceeding the WHO limit that around 60 million individuals are at the risk of As mediated toxicity. This entails that total number of samples are too low to ‘predict and claim’ human hazard on a very large scale that covers Punjab and Sindh provinces (the whole Indus Valley). Rather than considering a truly spatially resolved area, the majority of groundwater samples were taken from areas near to the River Indus, which are most likely to have As contamination. Moreover, their study claimed the impact of As hazard for overall population of Pakistan is unrealistic and an overestimation of the As-affected population, while various small specific location-based studies at village level have observed the high concentrations of As in groundwater, primarily in both Sindh and Punjab provinces (Table 2). According to Rahman et al. 1997, the maximum 80 µg/L concentration of As in groundwater of Karachi was reported that exceeded the allowable limits 10 and 50 µg/L, respectively, devised by WHO and Pakistan Standards and Quality Control

Authority (PSQCA). Due to consumption of As-contaminated groundwater, around 13–16% of population of Sindh and 23% population of Punjab province severely at risk. Ahmad et al. 2004 reported As level in ranged from 10 to 50 µg/L. A study was conducted by (Farooqi et al. 2007a) in Kalalanwala, Kasur Lahore Punjab and reported the maximum concentration of As in groundwater as 2400 µg/L. While Nickson et al. 2005 reported the maximum concentration of As at 400 µg/L in groundwater of Muzaffargarh, and 1000 µg/L in Multan. Recently, a study was conducted by Shakoor et al. 2018 and tested around 123 wells from five diverse locations in Punjab, i.e., Multan, Bahawalpur, Rahim Yar Khan, Vehari, and Chichawatni. This study reported As level ranges from 1.2 to 206 µg/L, and the mean concentrations of As were in the following order 120 > 72 > 53 > 22 > 9 µg/L, respectively, reported for Chichawatni > Multan > Bahawalpur > Vehari > Rahim Yar Khan. As concentration in 75% of groundwater samples were exceeding than the WHO defined standards of As in drinking water and around 41% wells were reported higher than Pakistan National Environmental Quality Standards (NEQS). Rasool et al. (2016b) and Shakoor et al. (2018) reported the indication of the oxidizing conditions prevailing in groundwater in terms of the higher levels of  $\text{SO}_4^{2-}$ ,  $\text{Cl}^-$ ,  $\text{CO}_3^{2-}$ , alkaline pH and high EC that resulted in abundance of As(V) species and suggested that the oxidative dissolution is the main process dominant in Multan District aquifer that release of As in groundwater. The similar type of study was conducted by Tabassum et al. 2018, which reported the mean value of As in Hasilpur at 9 µg/L and the maximum value of As at 100 µg/L. The oxidative dissolution possible mechanism As release in aquifer. In another study conducted by Rasool et al. 2016a, 44 groundwater samples collected from Mailsi were analyzed and reported  $\text{HCO}_3^-$  and  $\text{Cl}^-$  and  $\text{Ca}^{2+}$  as the dominant ions, and overall water chemistry of the Mailsi was  $\text{CaMgHCO}_3^-$  type. The As concentrations were ranged from 11 to 828 µg/L. Another study was conducted by Mushtaq et al. 2018, Lahore, Kasur district, and this study reported As in groundwater ranged between below detection limit (BDL) 2–548 µg/L with 59% samples beyond the WHO permissible limit and around 31% samples having higher level than the NEQS devised by Pakistan. In partially oxidizing aquifers, the mean level of  $\text{NO}_3^-$

**Table 2** Spatial distribution of As ( $\mu\text{g/L}$ ) in groundwater, major anions/cations and anthropogenic/natural sources of As Pakistan scenario

Province name	Location name	Major cations and anions composition	Sources anthropogenic and natural	As concentration (min -max) ( $\mu\text{g/L}$ )	References
Sindh	Tharparkar	High pH, $\text{Ca}^{2+}$ , $\text{Na}^+$ , $\text{NO}_3^-$ , $\text{Cl}^-$ , $\text{SO}_4^{2-}$ , $\text{PO}_4^{3-}$ , and $\text{HCO}_3^-$	Arid environment, complex geology with several process and reductive dissolution	100–2580	Brahman et al. (2013)
	Nagar Parker	pH neutral to alkaline, $\text{Na}^+$ , $\text{Ca}^{2+}$ , $\text{HCO}_3^-$ and $\text{PO}_4^{3-}$	Several geological factors	0–360	Rafique et al. (2009)
	Karachi	pH neutral to alkaline, high TDS	Not defined	Bdl to 80	Ali et al. (2013)
	Coastal area Karachi	pH neutral to alkaline, high TDS	Not defined	Bdl to 8	Rahman et al. (1997)
	Manchar Lake adjacent areas	pH neutral	Not defined	0–96	Arain et al. (2009b)
	Jamshoro	pH neutral, $\text{Ca}^{2+}$ and $\text{Mg}^{2+}$ , $\text{Na}^+$ , $\text{HCO}_3^-$ and high TDS	Not defined	0–106	Baig et al. (2009)
	Tando Allah Yar	pH is acidic to alkaline, Fe, Zn, Pb, Ni and Mn	Anthropogenic sources	Bdl to 5.48	Jabeen et al. (2014)
	Hyderabad	pH neutral, $\text{Ca}^{2+}$ and $\text{Mg}^{2+}$	Not defined	0	Baig et al. (2009)
	Khairpur (Mirs)	pH neutral	Not defined	7–98	Baig et al. (2011)
	Khairpur (Mirs)	pH neutral	Alluvial deposit Indus river	8.8 (mean)	Rabbani et al. (2017)
	Over all district Khairpur (Mirs)	pH neutral	Alluvial deposit Indus river	0–350	Rabbani et al. (2017)
	Thari Mirwah	pH neutral	Alluvial deposit Indus river	6.65 (mean)	Rabbani et al. (2017)
	Thari Mirwah	pH neutral	Not defined	18–40	Baig et al. (2011)
	Kotdigi	pH neutral	Not defined	0–12	Azizullah et al. (2011)
	Kotdigi	pH neutral	Alluvial deposit Indus river	1.09 (mean)	Rabbani et al. (2017)
	Dadu	pH neutral	Not defined	0–11	Azizullah et al. (2011)
	Sobo Dero	pH neutral	Alluvial deposit Indus river	24.4 (mean)	Rabbani et al. (2017)
	Kingri	pH neutral	Alluvial deposit Indus river	27.6 (mean)	Rabbani et al. (2017)

**Table 2** continued

Province name	Location name	Major cations and anions composition	Sources anthropogenic and natural	As concentration (min -max) ( $\mu\text{g/L}$ )	References
	Faiz Ganj	pH neutral	Alluvial deposit Indus river	2.70 (mean)	Rabbani et al. (2017)
	Johi	pH neutral	Not defined	0–10	Azizullah et al. (2011)
	Sehwan	pH neutral	Not defined	0–10	Azizullah et al. (2011)
	Gambat	pH neutral	Not defined	0–11	Jabeen et al. (2014)
	Gambat	pH neutral	Alluvial deposit Indus river	24 (mean)	Rabbani et al. (2017)
Punjab	Lahore and Kasur	$\text{Na}^+$ , $\text{SO}_4^{2-}$ , $\text{HCO}_3^-$ , $\text{F}^-$ and high pH	Natural and anthropogenic sources, coal burning, air pollutants and at high pH desorption process	0–2400	Farooqi et al. (2007a)
	Kasur	$\text{Na}^+$ , $\text{SO}_4^{2-}$ , $\text{HCO}_3^-$ and high pH	Natural and anthropogenic sources, agricultural activities, industrial waste and at high pH desorption process	Bdl to 548	Mushtaq et al. (2018)
	Rahim Yar Khan	pH neutral, $\text{PO}_4^{3-}$ and $\text{Fe}^{2+}$	Reductive dissolution of Iron hydroxides natural source	150–400	Haque et al. (2008)
	Muzaffargarh	pH neutral to alkaline, $\text{Na}^+$ , $\text{Ca}^{2+}$ , $\text{HCO}_3^-$ , $\text{SO}_4^{2-}$ , $\text{Cl}^-$ and $\text{PO}_4^{3-}$	Reductive dissolution of Iron hydroxides natural source	0–400	Nickson et al. (2005)
	Multan	pH neutral to alkaline, $\text{Na}^+$ , $\text{Ca}^{2+}$ , $\text{HCO}_3^-$ , $\text{SO}_4^{2-}$ , $\text{Cl}^-$ and $\text{PO}_4^{3-}$	Reductive dissolution of Iron hydroxides natural source	0–1000	Nickson et al. (2005)
	Mailisi	pH neutral to alkaline, $\text{Na}^+$ , $\text{Ca}^{2+}$ , $\text{HCO}_3^-$ , $\text{Mg}$ , $\text{SO}_4^{2-}$ , $\text{Cl}^-$ and $\text{PO}_4^{3-}$	Evaporative enrichment of salts and rock–water interaction	10–750	Rasool et al. (2016b)
	Hasilpur	pH neutral to alkaline, $\text{Na}^+$ , $\text{Ca}^{2+}$ , $\text{HCO}_3^-$ , $\text{Mg}$ , $\text{SO}_4^{2-}$ , $\text{Cl}^-$ and $\text{PO}_4^{3-}$	Evaporative enrichment of salts, agricultural activities	0–100	Tabassum et al. (2018)
	Jhelum	pH neutral	Coal mining activities and geothermal source	0–50	Iqbal (2001)
	Chakwal	pH neutral	Coal mining activities and geothermal source	0–25	Iqbal (2001)
	Multan district adjacent areas	pH neutral to alkaline	Reductive dissolution pH, salinity, Fe and $\text{CO}_3$ controlling As the release	1.2–206	Shakoor et al. (2018)
Khyber Pakhtun Khwah (KPK)	D.G Khan	pH neutral to alkaline, $\text{Na}^+$ , $\text{Ca}^{2+}$ , $\text{K}^+$ , $\text{HCO}_3^-$ , and $\text{SO}_4^{2-}$ ,	Reductive dissolution of Iron hydroxides natural source and Metals leaching from Mine Wastes	0–29	Malana and Khosa (2011)
	Jijal Dubair	pH neutral, $\text{Ca}^{2+}$ , $\text{Mg}^{2+}$ and $\text{HCO}_3^-$	Not defined	0–17	Muhammad et al. (2010)

**Table 2** continued

Province name	Location name	Major cations and anions composition	Sources anthropogenic and natural	As concentration (min -max) (µg/L)	References
	Besham	pH neutral, Ca <sup>2+</sup> , Mg <sup>2+</sup> and HCO <sub>3</sub> <sup>-</sup>	Not defined	0–0.5	Muhammad et al. (2010)
	Jijal Dubair	pH neutral, Ca <sup>2+</sup> , Mg <sup>2+</sup> and HCO <sub>3</sub> <sup>-</sup>	Not defined	0	Muhammad et al. (2010)
Northern Areas	Kohistan	Ca <sup>+</sup> , Mg <sup>2+</sup> , Na <sup>+</sup> , SO <sub>4</sub> <sup>2-</sup> , Cl <sup>-</sup> and Fe	Natural geological sources (mafic and ultra-mafic rocks)	0.13–17	Muhammad et al. (2010)
All Pakistan	Sindh, Punjab, Baluchistan, KPK (No. of samples 1184)	pH neutral to alkaline, Na <sup>+</sup> , Ca <sup>2+</sup> , HCO <sub>3</sub> <sup>-</sup> , Mg, SO <sub>4</sub> <sup>2-</sup> , Cl <sup>-</sup> and Fe	Natural and anthropogenic sources, agricultural activities, industrial waste and at high pH desorption process	0–500	Podgorski et al. (2017)

*Bdl* below detection limit

reported at 8 mg/L and moderate to high level of SO<sub>4</sub><sup>2-</sup> average at 244 mg/L, coupled with Eh values of 113–402 (mV) and alkaline pH of 7.3–8.8. Similarly, the highest level of As was reported at 2580 µg/L in Tharparkar, Sindh (Brahman et al. 2013). While (Arain et al. 2009a) reported the maximum As concentration in groundwater of the adjacent locations of Manchar lakes ranging from 23.3 to 96.3 µg/L. According to the published literature, the concentrations of As in the various parts of Pakistan such as Jamshoro and Kohistan regions were reported high, i.e., 100 µg/L (Baig et al. 2009; Muhammad et al. 2010). Another study was conducted by Malana and Khosa 2011, and the maximum concentration of As in groundwater was reported at 29 µg/L. In Table 2, overall As distribution, sources and environmental factors that control As concentration in groundwater of Pakistan are summarized.

**Mechanism of Arsenic contamination in Pakistan: a comparison with worldwide literature**

The redox conditions of an aquifer system play a significant role in the release of As from sediments to groundwater (Smedley and Kinniburgh 2002). The comparison of elevated level As in groundwater worldwide under various redox conditions is given

in Table 3 with worldwide, and Pakistan data of redox-sensitive species shown in Fig. 4 and Table 3 indicate Pakistan groundwater prevailing oxidizing conditions; the groundwater contains a higher concentration of SO<sub>4</sub><sup>2-</sup>, NO<sub>3</sub><sup>-</sup>, and SO<sub>4</sub><sup>2-</sup>, HCO<sub>3</sub><sup>-</sup> and alkaline pH with low Fe and Mn. In (Fig. 4) Bivariate plot of As versus pH comparison literature showed that in Pakistan, the maximum As concentration reported at pH ranges 7–7.5 same as Bangladesh (Anawar et al. 2003), and comparison within countries, the (Figure S1) same conditions are reported (Nickson et al. 2005; Arain et al. 2007). The As versus EC biplot showed that As concentrations dominated at the sampling sites that exhibited lower EC values especially in South Asian countries, which implied a negative correlation between the levels of As and EC values. In Pakistan, the EC increases from 3000 µS/cm which indicates the As concentration decreases with an increase EC (Nickson et al. 2000; Stüben et al. 2003; Farooqi et al. 2007a; Bibi et al. 2008; Mukherjee and Fryar 2008; Halim et al. 2009; Krishna et al. 2009; Kumar et al. 2010; Rasool et al. 2015). Bivariate plot of As versus SO<sub>4</sub><sup>2-</sup> comparison with an extensive literature, in Pakistan, shows the maximum As concentration dominant at range 100–1000 mg/L and seems the same condition as compared with China, Argentina and Spain while comparing within country regions (Fig. 4); the situation is much like Lahore

**Table 3** Comparison of high As concentration in groundwater under various redox conditions with the dominant type of As species in the aquifer system

Groundwater environmental conditions	As-contaminated groundwater hydrological characteristics	As dominant species	As mobilization mechanism	As-affected countries
Reducing environment having pH lower to neutral (6–7.2) and very low Eh (mv) value	High Fe > 1 (mg/L), high Mn > 0.05 (mg/L), low level of $\text{SO}_4^{2-}$ < 5 (mg/L), $\text{NO}_3^-$ < 1 (mg/L) with higher concentration of $\text{NH}_4^+$ > 1 (mg/L), $\text{HCO}_3^-$ > 500 (mg/L) and presence of organic matter	As(III)	In the presence of organic matter Reductive dissolution of iron oxy-hydroxide (FeOOH) result of that release of arsenic in groundwater	India, Bangladesh, Nepal, China, Hungary and Vietnam
Oxidizing environment having pH (7–9) slightly alkaline to strongly alkaline	High level of $\text{HCO}_3^-$ > 500 (mg/L), high salinity (evaporative condition) and low level of (Fe and Mn)	As(V)	Arsenic desorption from metal oxide surface under high pH, evaporative control on As level in (arid and semiarid regions)	Argentina, Spain, USA, Pakistan and Mexico.

Kasur. An overall trend showed that Sindh groundwater contained the lower concentration of  $\text{SO}_4^{2-}$  as compared to Punjab, while the nitrite concentration is high due to the infiltration of agriculture runoff in subsurface groundwater water environment (Nickson et al. 2005). The Mn concentration in groundwater reflects reducing condition of the subsurface environment in Bangladesh and India. These both countries have same process for Mn mobilization in groundwater; which could be attributed to early stage degradation of organic matter and availability of the reducing conditions that ultimately assist As linkage to Mn (Nickson et al. 2000; Stüben et al. 2003). In Pakistan, the maximum As concentration reported at low Mn concentrations that reflect low reducing conditions prevailing in Pakistan. Though As versus nitrate plot shows the maximum As concentration reported between the range 1–10 mg/L, Argentina, Spain, Bangladesh, India and Pakistan have the same type of nitrate concentration, while in China, the maximum As concentration reported at lower nitrate concentration. However, in Bangladesh, China, Pakistan, Spain and Argentina, bivariate plot of As versus bicarbonate shows the As concentration dominant at ranged from 100 to 1000 mg/L.

### Groundwater recharge and its effects on Arsenic concentration

The various biogeochemical reactions are happening in groundwater. The stable isotopic techniques are

useful to trace the origin and sources of dissolved minerals and their constituents in groundwater (Kendall 1998; Cook and Herczeg 2012). However,  $\delta^2\text{H}$  and  $\delta^{18}\text{O}$  composition in the hydrological process is used to understand the origin of water and integration of water in the subsurface environment, and isotopic evidence is widely used as tracers of the diverse hydrological process going on in the environment (Clark and Fritz 1997). The As is an oxyanion-forming element that persists in nature, and its mobility is high under redox conditions as compared with other oxyanion-forming elements such as chromium, vanadium, molybdenum, and selenium (Smedley and Kinniburgh 2002). However, some studies have used the stable  $\delta^2\text{H}$  and  $\delta^{18}\text{O}$  isotopic compositions of As-contaminated water as to understand groundwater recharge sources and its effect on the As mobilization in groundwater (Mukherjee et al. 2007; Aziz et al. 2009; Xie et al. 2012; Mladenov et al. 2014). Previous studies conducted on aquifers in Texas, USA and at Inner Mongolia, China revealed that the concentrations of As change with the groundwater flow path (Haque and Johannesson 2006; Guo et al. 2010). The same kind of results also proposed by Stüben et al. 2003 and Rowland et al. 2011 that the concentration of As significantly varied along the groundwater flow as of recharge to discharge in the study areas. In Cambodia, according to Polizzotto et al. 2008, the mobilization of As from lower sediments is due to the changing in surface hydrological process and change in groundwater flow. In Table 4, the worldwide list of studies shows the



**Fig. 4** Countries facing As contamination in groundwater under various redox conditions worldwide comparison bivariate plots of As versus pH, EC (µS/cm), SO<sub>4</sub><sup>2-</sup> (mg/L), NO<sub>3</sub><sup>-</sup> (mg/L), HCO<sub>3</sub><sup>-</sup> (mg/L) and Mn (mg/L)

applications of δ<sup>2</sup>H and δ<sup>18</sup>O isotopic compositions of As-contaminated groundwater and its impacts on the various hydrological process on As level. In Pakistan, Lahore and Kasur district, a study conducted by Mushtaq et al. 2018 employs isotopic δ<sup>2</sup>H and δ<sup>18</sup>O data that revealed the low concentration of As at ≤ 10 µg/L, the medium concentration at

11–50 µg/L and the highest concentration at > 50 µg/L in the contaminated groundwater, implying that the evaporation controls also the main cause for enriched As in groundwater.

## Mitigation measures and technologies

Multiple alternative technologies have been defined and verified for water supply in numerous regions of Pakistan and globally to reduce the levels of As in drinking water. The different As elimination techniques generally based on following six defined principles: the first is employing the adsorption process, the second is using the membrane tools for filtration and purification, the third is oxidation process, the fourth biological oxidation using microorganisms to oxidize As(III) to As(V) through the removal Fe and Mn oxides, the fifth is ion exchange via anion and cation exchange resins, and the sixth is co-precipitation as well as oxidation of As(III) to As(V). Moreover, the As(V) can also be removed through sedimentation, filtration and coagulation. Numerous As treatment technologies need pH modification for better performance, which directly influence the speciation of As in uncooked water (Bissen and Frimmel 2003). Similarly, sorption as removal process is also very sensitive to pH because in most of the media types pH is reported to be greater than 8.5, which reduced the adsorption capacity of the media (Wang et al. 2004) and accordingly enhanced the cost of single-use media. Besides chemical oxidation, some bacterial species applied in groundwater that also performed the catalysis of As through oxidative process (Jain and Singh 2012). This method used usually applied on aquifer that contains significant levels of Mn and Fe in the sediments (Jain and Singh 2012). Fe and Mn oxidizing bacteria can convert As(III) to As(V) that naturally exists in groundwater. The As could remove through co-precipitation and adsorption. The efficiency of As removal determined through As and Fe ratios as well as the initial level of Fe. On the other hand, ferric coagulant was also added initially for efficient removal of As, and then, this process became independent with the pH varying between 5.5 and 8.5 (Violante et al. 2006; Bibi et al. 2015). Moreover, the condition for development of aluminum arsenate precipitates reported to ideal in neutral to alkaline systems (Violante et al. 2006). Nevertheless, high level of orthophosphates, organic matter, and silicates decline the efficiency of precipitation because it increased the competition for sorption sites (Fields et al. 2000a, b). Many studies likewise described As sorption on chemical oxidation and oxides of Mn (Tournassat et al. 2002). In

Bangladesh, Hug et al. 2001 investigated the solar oxidation process and established a convenient method for the removal of As at neutral pH in drinking water via using locally available sources, without application of any additional chemicals and other pH alteration. Due to the natural oxidation, the reduction in concentration of As was also detected during water collection and storage in tanks at household level (Ahmed 2001). In Bangladesh, exploration has been carried out to remove As through sedimentation that was reported to be dependent upon Fe precipitation (Ahmed 2001). This study further revealed that the sedimentation process reduced As content by more than half like, 380–480 µg/L in water samples obtained from As-contaminated well, containing CaCO<sub>3</sub> and Fe (8–12 µg/L); however, the desired As removal rates were not achieved (Ahmed 2001). However, many studies reported the As concentration reduction through sedimentation process was 0–25%. Mostly, passive sedimentation has been recommended as an unsuccessful approach to achieve the desired level of As (Kinniburgh and Kosmus 2002). The phytoremediation study is based on potential uptake of As by two Cyperaceae spp. the *Schoenoplectus americanus* and *Eleocharismacrostachya*, collected in the vicinity of Chihuahua, Mexico (Bundschuh et al. 2010). Interestingly, both of the plant species were able to survive at high levels of As and could be efficiently used for hemofiltration because 97% of the plant species bear As load without any significant influence on growth of plant (Bundschuh et al. 2010). The explored desiccated microalgae *Spyrogira* spp. for the removal of As from an acid mine drainage, and 80–90% removal was consummated within 4 days. Many of the marine plant species, *Ranunculus trichophyllus*, *Saniculifolius*, *Ranunculus peltasts* spp., *Azollacaroliniana*, and leaves of *Juncus effuses* all exhibited a very high potential for As-phytofiltration, while they declared useful for treatment of natural water bodies and constructed wetlands (Parmar and Singh 2015). The comparatively efficient alternative method for As removal is the biological oxidation of Fe and Mn. As usually contaminates groundwater under reducing condition in the presence of abundant supplies of Mn and Fe. Therefore, filters enriched with bacteria are used for removal of Mn and Fe and such bacterial retain potential to finally oxidized As(III). Recently, the microbial treatment of water was observed to result in mineral oxide formation; this



**Table 4** Worldwide stable isotopic applications to investigate factors controlling levels of arsenic in groundwater contamination

Country names	Locations	Isotopic compositions used	Geochemical process investigations	Effects on As concentrations (Yes/No)	References
Pakistan	Lahore-Kasur	$\delta^{18}\text{O}$ , $\delta^2\text{H}$ and $\delta^{34}\text{S}$	Sulfate level and groundwater recharge	NA	Farooqi et al. (2007a)
	Kasur	$\delta^{18}\text{O}$ and $\delta^2\text{H}$	Water evolution and groundwater recharge	Yes	Mushtaq et al. (2018)
Bangladesh	Meghna Basin	$\delta^{18}\text{O}$ and $\delta^2\text{H}$	Groundwater recharge	Yes	Hasan et al. (2009)
	Bangladesh	$\delta^{18}\text{O}$ , $\delta^3\text{H}$ and $\delta^2\text{H}$	Water evolution and groundwater recharge	Yes	Stute et al. (2007)
India	Bengal Basin	$\delta^{18}\text{O}$ and $\delta^2\text{H}$	Recharge	Yes	Mukherjee et al. (2007)
	West Bengal	$\delta^{34}\text{S}$ , $\delta^{18}\text{O}$ and $\delta^2\text{H}$	Sulfates level and groundwater recharge	Yes	Stüben et al. (2003)
	West Bengal	$\delta^{34}\text{S}$ , $\delta^{18}\text{O}$ and $\delta^2\text{H}$	Groundwater recharge, discharge and river water interaction	Yes	Mukherjee et al. (2007)
China	Minqin Basin	$\delta^{18}\text{O}$ , $\delta^2\text{H}$ and $^{13}\text{C}$	Age and groundwater recharge sources	NA	Zhu et al. (2007)
	Datong Basin	$\delta^{18}\text{O}$ and $\delta^2\text{H}$	Groundwater recharge and discharge	Yes	Xie et al. (2012)
	Yinchuan Basin	$\delta^{18}\text{O}$ and $\delta^2\text{H}$	Evaporation effects	No	Guo et al. (2014)
	Songnen Basin	$\delta^{18}\text{O}$ , $\delta^2\text{H}$ and $\delta^{13}\text{C}$	Groundwater flow path and organic content in water	Yes	Guo et al. (2014)
	Inner Mongolia	$\delta^{18}\text{O}$ and $\delta^2\text{H}$	Water–Rock interaction and groundwater recharge	Yes	Mukherjee et al. (2009)
	Inner Mongolia Hetao Plain	$\delta^{18}\text{O}$ , $\delta^2\text{H}$ and $\delta^{34}\text{S}$	Groundwater recharge, discharge and sulfates reduction	Yes	Hasan et al. (2009)
	Inner Mongolia Hetao Plain	$\delta^{18}\text{O}$ , $\delta^2\text{H}$ and $\delta^{\text{Sr}}$	Rock weathering and evapotranspiration	Yes	Deng et al. (2009)
Argentina	Argentina	$\delta^{18}\text{O}$ , $\delta^2\text{H}$ , $\delta^{34}\text{S}$ and $\delta^{14}\text{C}$	Groundwater recharge, age and Pyrite weathering	No	Smedley et al. (2002)
Maine	Goose River	$\delta^{18}\text{O}_{\text{so}_4}$	Oxidation of Arsenian pyrite	Yes	
Hungary and Romania	Hungary and Romania	$\delta^{18}\text{O}$ , $\delta^2\text{H}$ , $\delta^{13}\text{C}$ , $\text{CH}_4$ , and $\delta^7\text{Li}$	Groundwater recharge, rock–water interaction and geothermal influences	Yes	Rowland et al. (2011)
Vietnam	Hanoi Area	$\delta^{18}\text{O}$ and $\delta^2\text{H}$	Groundwater recharge and surface water interaction	Yes	Berg et al. (2008)
China/Taiwan Province	Chia Nan Plain	$\delta^{18}\text{O}$ and $\delta^2\text{H}$	Rock–water interaction	Yes	Nath et al. (2008)

**Table 4** continued

Country names	Locations	Isotopic compositions used	Geochemical process investigations	Effects on As concentrations (Yes/No)	References
Botswana	Okavango Delta	$\delta^{18}\text{O}$ and $\delta^2\text{H}$	Groundwater flow and evapotranspiration	Yes	Mladenov et al. (2014)

NA not applicable

process can efficiently remove. The formation of Mn(III/IV) oxides contribute to the abiotic oxidation of As(III) and immobilization of As(V) through sorption to Fe(III) oxides (Nitzsche et al. 2015a, b). Another study also reported the removal of As from groundwater through biological oxidation Fe and Mn, albeit without any specific oxidizing agents (Kouras et al. 2007). The amount of oxidation induced by bacteria for As(III) to As(V) removal is significantly higher than Mn oxides added abiotic oxidation (Kouras et al. 2007). Bacterial strains play an essential role in As(III) oxidation and generation of Mn-oxide surfaces for the removal of dissolved As(V) and As(III). The co-precipitation to treat As contamination water is intensively used technique in many pilot-scale studies. Chemical precipitation usually includes three processes such as lime softening, microfiltration and coagulation filtration by gravity (Chwirka et al. 2000; Sancha 2006). The lime softening used only for As removal has limitations such as cost-effective or economical. However, lime softening is useful for removing hardness from water, so further this process increased removal of As Likewise, As removal is also achieved through addition of lime which leads to the increase in pH level up to 10.5. At this pH range, the hydroxide precipitates out, and Mn and As remove through co-precipitation. Further, the coagulation-based microfiltration also employed the similar coagulation methods with modification of granular media filtration. In this methods the membrane is subjected to backwash periodically for the removal of solids and repair of its hydraulic capacity (Thirunavukkarasu et al. 2003). The novel approaches for treatment of As-contaminated water are continuing to be investigated, predominantly to employ the applicable methods that could have significant impact on As removal from drinking water in developing communities. The combination of ferric salt and cactus mucilage was examined as a flocculation combination that can be

used as coagulant structure for As removal. Adsorption-based techniques have been widely employed to treat As-polluted groundwater, which can minimize As concentration to 10  $\mu\text{g/L}$ . The efficiency of this process was affected by various factors such as raw water features and contaminants. Further, these column packed media usually used for adsorption. Contaminated water passed through the column to catch and adsorb pollutants, while adsorption locations influence the threshold filtration; therefore, the column must restore and change with newly developed media. Frequently recommended adsorption media for the removal of As include filters, sand coated with iron, granular ferric-hydroxide, activated alumina, and other different mixed adsorbents.

## Conclusion and recommendations

The elevated As in groundwater is a major problem for human health and agriculture. This review encompasses the latest development in scientific understanding based on various interdisciplinary investigations, which highlighted the status of As contamination in the environmental matrices, mechanisms, mobilization in groundwater, and its biogeochemical relations, and advancements in the remediation strategies. Globally, the biogeochemical processes mainly caused the dissolution of naturally occurring As into the groundwater sources. In Pakistan higher levels of  $\text{SO}_4^{2-}$ , Cl and  $\text{CO}_3^{2-}$  attached with high EC and basic pH and abundance of As(V) were an indication of the oxidizing conditions prevailing in groundwater. The oxidative dissolution is the dominant process of As release into Pakistan aquifer. Up to 2018, the 11 districts of Pakistan Sindh and Punjab provinces had been found As contamination in groundwater beyond the WHO and National standard level (10 and 50  $\mu\text{g/L}$ ). Tharparkar, Hyderabad along Indus River (Sindh)

districts and Lahore-Kasur (Punjab) are well-known hotspots of natural geogenic As contamination in drinking water extracted from aquifers. The current review not only highlighted the problem of As contamination worldwide but also revealed the recent epidemiology cases and toxicity mechanisms induced by As exposure under various redox conditions. The groundwater recharge mechanisms, isotopic evidence and its effects on As contamination in Bangladesh, India, China, Maine, Hungary, Vietnam and Botswana defined their positive impacts of groundwater recharge on As contamination. Most of numerous present methods for As removal include the direct removal of As converting As(III) to As(V) followed by As removal. The different efficient methods should be modified for pilot-scale application to successfully remove As by reducing operating and preservation cost. However, traditional processes of treatment such as lime softening, coagulation filtration, membrane filtration and Fe and Mn oxidation have employed for the removal of As contaminations in most of water treatment plants. Till now, several methods are at the initial experimental stages, and some have not got recognition at full scale. Further, extensive research is warranted for in-depth understanding of the origin, presence and As distribution patterns. In case Pakistan, the number of As poisoning cases are alarmingly severe that demonstrates the urgent and need for comprehensive testing of all drinking water sources in Indus Plain regions and proper mitigation measures should be recommended for the purpose of rehabilitation. The government and NGOs should vigilantly monitor the industrial and agricultural emissions that lead to As pollution into consumable water resources. At last, the present study will prove very helpful regarding diverse As mitigation measures at both national and regional level in near future and for better understanding the status of As pollution, categorizations of hydrological controls and As mobilization in both ground and surface water.

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## Compliance with ethical standards

**Conflict of interest** The authors declare that they have no conflict of interest.

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