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Current Situation of Aqueous Arsenic Contamination in Pakistan, Focused on Sindh and Punjab Province, Pakistan: A Review

Sanjrani MA[1]*, Teshome Mek[1], Sanjrani ND[2], Leghari SJ[3], Moryani HT[4] and Shabnam AB[5]

[1]*School of Resource and Environmental Engineering, Wuhan University of Technology, Wuhan, P.R. China*
[2]*School of Materials Science and Engineering, Wuhan University of Technology, Wuhan, P.R. China*
[3]*School of Soil and Water Sciences, College of Resources and Environmental Sciences, Agricultural University, Beijing, P.R. China*
[4]*School of Environmental Studies, China University of Geosciences, Wuhan, P.R. China*
[5]*Institute of Chemistry, University of Sindh Jamshoro, Pakistan*

Abstract

The arsenic contamination has seriously affected public health in Pakistan, especially in highly contaminated Sindh and Punjab provinces. Results of recent studies show that over 3% of the population in Punjab was exposed to arsenic contamination of over 50 ug/L in drinking water, and 20% of the population is exposed to over 10 ug/L, with the limited standard of WHO, same as the EPA also sets the maximum contaminant level goal (MCLG) for drinking water. The situation in Sindh province was worse than in Punjab province, as the results show that 16% and 36% of population exposed to arsenic contaminated water over 50 ug/L and 10 ug/L respectively. According to a study conducted and based on samples from 1,184 wells across the country that actually proved that the process of boiling or filtration was not helpful to remove As from groundwater. Recent medical studies have confirmed 40 cases of arsenicosis occurred in worst situation. The purpose of this paper is to make a review about the current situation of arsenic contamination and its effect in the Pakistan.

Keywords: Aqueous As contamination; Drinking water; Sindh; Punjab; Pakistan

Introduction

Though water pollution is a historical problem around the world, science has found solutions. During 1960's, both groundwater and surface water interaction studies were hot issues and researches were firstly focused on interaction between water in lakes and its groundwater in selected areas [1]. Usually the interaction between groundwater and surface water can be integral particular process in the areas of watersheds and governed by many factors including surface topology, geology, climate and ecosystem [2]. Later during 1970's, groundwater pumping in many areas was identified which have influenced "in-stream" flows and then a number of studies were conducted about the hyporheic zone is the transition zone between surface water in streams/rivers and groundwater [3]. More recently, the interaction between groundwater and surface water along river corridors was interested for the research groups due to ecological and climatic concerns and new technologies were being used to find out solutions of contamination water problems [4,5]. During the 1990s, long-term exposure ground water contaminated with As was cited as the most widespread threat to human health [4]. Arsenic contamination of groundwater is a form of groundwater pollution which is often due to naturally occurring high concentrations of arsenic in deeper levels of groundwater (Wikipedia, 2017). Extensive scientific studies were investigated into the geochemical processes, resulting in high As level of concentration in groundwater almost all over the world [6-9]. During this period naturally occurring As was found to be widespread in groundwater [10]. Arsenic contaminated groundwater has caused problems among millions of human beings in many regions around the world, especially in Asian countries including Bangladesh, India, Cambodia, Vietnam, China and recently also Chinese Taiwan, also found in Hungary, Chile and Argentina [8,11]. Sources of exposure of As was proved to be natural from the earth's crust and widely distributed throughout the environment in the air, water and land. It can enter the water supply from natural deposits in the earth or from industrial and agricultural pollution as highly toxic in its inorganic form [6]. As could play a role in the development of cancer, vascular disease and lung disease, recently many cases of diabetes developed by As confirmed by medical agencies and Epidemiological survey by UNICEF in 2016 [12]. The Food and Drug Administration confirmed that long-term exposure to high levels of arsenic is associated with higher rates of skin cancer, bladder cancer and lung cancer, as well as heart disease. As this review study focuses on Pakistan water issues, researchers are focusing on the water problem related to India and Bangladesh for the water relationship with Pakistani. Both Pakistan and India had historically subsidized electricity and diesel for running agricultural wells that tap into the aquifer. Groundwater users only pay for the energy used to mine the resource; the water itself is not metered or priced. The aquifer is literally free for anyone to tap into by drilling a well-whether it is for agricultural, industrial or domestic purposes [13]. Both countries are taking out far more water than replenished by rain or rivers. In fact, India extracted more groundwater than any other countries in the world (not just from the Indus), and Pakistan was the fourth in the list. The Indus aquifer was already the second most "overstressed" groundwater basin in the world and at the current rates of use, reserves like this may be "severely depleted" over the next few decades [14].

Aqueous Arsenic Contamination in Pakistan

Recently, arsenic risk in Pakistan was much serious than expected. Alarmingly high levels of As in Pakistan's ground water also in surface water have been found [15]. It is recently reported that more than 50

***Corresponding author:** Manzoor Ahmed Sanjrani, School of Resource and Environmental Engineering, Wuhan University of Technology, China, Tel: 008615623306227/00923453720744; E-mail: manzoor.geo@gmail.com

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million people in Pakistan were at a risk of arsenic poisoning because most of Pakistani communities use groundwater for drinking and other households polluted with arsenic [16]. Previous studies of 1990's had revealed that groundwater in some areas of Pakistan also contained high levels of arsenic while the extent of those risks was still unknown [17]. The new study showed that 50-60 million people living in the Indus valley, around 95% of population in Pakistan rely on groundwater, which was very likely exceeds WHO safe level [18] for lack of awareness and no safety implementation. Now, a study suggested Pakistan might be grappling with its own arsenic emergency, with up to 60 million people exposed to contaminated water [19]. Arsenic level in many cities of Pakistan had been found a little worst (Figure 1) [14]. A systematic screening of groundwater for arsenic contamination started in Pakistan was relatively late in early 2000. In 2001, 35 districts were surveyed for arsenic contamination and drinking water sources. 8712 samples were collected and analyzed. 9% of the samples were found contain arsenic above WHO level 10 ug/L, whereas 0.70% samples were above 50 µg/L. 848 samples contained arsenic concentrations according to calculation. In 2003, another PCRWR team worked on it, ground water samples were collected at 1,184 sites throughout the country, taken from wells down into the Earth till 100 feet. The team then used statistical methods to construct a hazard map and to estimate the size of population exposed to the threat [16,20]. According to a study conducted by Podgorski et al. [16] and based on samples from 1,184 wells across the country actually proved that the process of boiling or filtration were not helpful to remove arsenic from groundwater. Some expensive procedures such as reverse osmosis should be dealt by government because these were beyond the reach of most poor people [16].

Actual data on arsenic concentration levels in drinking water was lack in Pakistan because around the Pakistan all communities except some big cities unusually dependant on a single, a larger underground natural reservoir aquifer covers an area of 160,000 km^2 and it is known as the Indus basin aquifer, probably larger than England. As it was reported that more than 50 million people in Pakistan were at a risk of arsenic poisoning because of using groundwater for drinking purpose. So next, the team created the region's first risk map for arsenic pollution in water, which showed the probability of dangerous concentrations around the country [16,21]. By estimating the communities relying on groundwater for drinking, the team reported that 50 to 60 million people might use water contain more than 50 mg/L of arsenic, five times the WHO guideline by coming year was no step carried out for the solution. The map is given in the Figure 2 to show the increased probability of arsenic concentrations [15,16].

The best methodology is "1 km by 1 km", Kazi et al. [22] team used as geographical country areas were divided as "1 km by 1 km". However, Geological distribution in underground water for arsenic was quite interesting to the researchers because within the same geographical areas, safe wells were found very near to the contaminated wells. Therefore, it was unfair to label the whole 1 km by 1 km area as exposed, based on one to two samples. But areas existing along the river were chosen according to map. The risk assessment based on GIS mapping

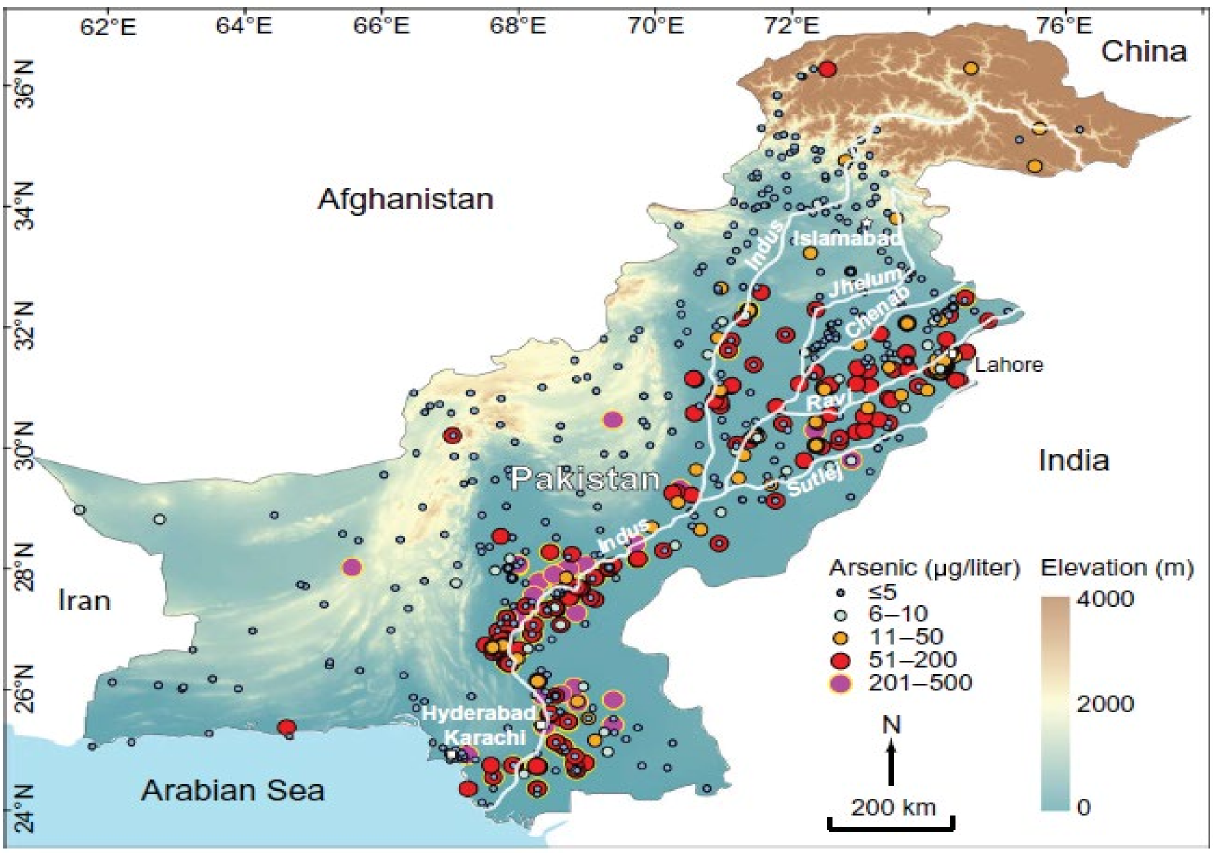

Figure 1: Arsenic concentrations measured in Pakistan groundwater [16].

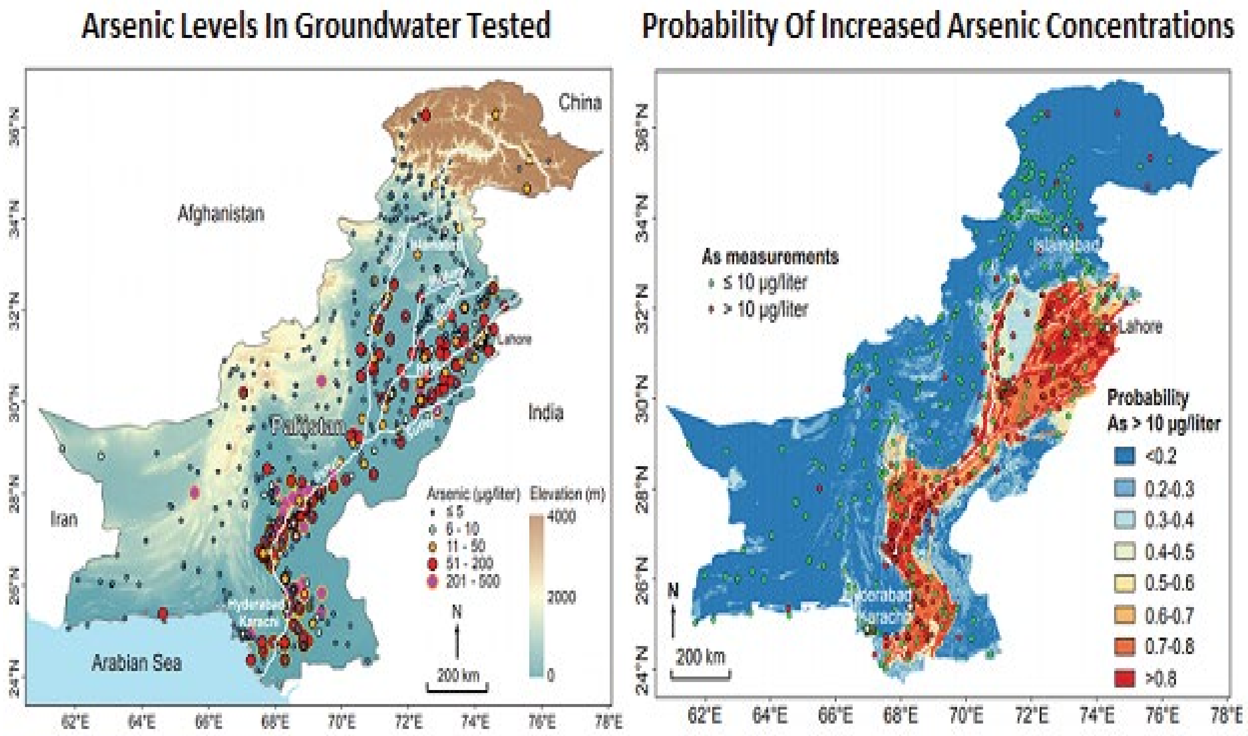

Figure 2: Hazard map probability [16].

showed that about 13 million people were likely to have arsenic exposure in Pakistan [15,20,23]. Arsenic concentration was found high in surface and ground water in Pakistan mainly in two provinces Punjab and Sindh. Water resources 3% and 16% with As contamination level of over 50 µg/L were reported in Punjab and Sindh, respectively, while 20% and 36% of water resources of Punjab and Sindh are contaminated with arsenic above 10 µg/L [15]. Further studies are being conducted to know the actual water problems and solutions in Sindh province.

Aqueous Arsenic Contamination in Sindh Province

In Sindh, arsenic distribution at depths of 10-150 feet more or less follows a similar pattern from water sources, showing groundwater was contaminated both shallow and deep [24] as 19,571 water sources were analyzed. However, no arsenic was observed in the depths over 150 feet resulting in this depth range, 99% of 69 water sources have no arsenic contamination while only one has contamination which was less than 10 ug/L. In Dadu city, different results were found when the shallow one had contamination over 100 ug/L while for the deep one was less than 10 ug/L in two sources [25]. The situation of arsenic with largest freshwater lake in Pakistan know to be Manchar lake situated in southern part of Sindh was found As concentrations in water with the range of 35.2-158 µg/L (the mean range is 97.5 µg/L), which was much higher than permissible limit of WHO. Similarly worse situation in surface water in Jamshoro city, Sindh that samples were observed to have highest content of As in surface water more than 50 µg/L [25,26].

Recently studies were carried out that the bodies belong to Indus were contaminated with lead and arsenic at considerable level, from the northernmost territory of Gilgit-Baltistan to the lower parts of Sindh [27], similarly communities belong to different areas of Pakistan facing severe public health problems related to As. Survey had been conducted about soil and it showed variations in surface and deep soils related to As concentrations in soil samples As was relatively higher in surface soils than deep soils even the samples were taken from the same location. The highest average As content was found to be 46.2 mg/kg in soils in the agricultural areas of Sindh (irrigated with As-rich lake water). In other survey it was concluded that sediments play a vital role for arsenic spreading in water bodies [28]. Total As level in sediment and soil irrigated with lake water in some parts of the Sindh was higher than the threshold effects level as reported by interim sediment quality assessment values and USEPA. The mean values of total As were found in the range of 11.3-55.8 µg/L in Manchar lake sediment in Sindh province [27]. The cities in Sindh, Khairpur, Gambat, Kotdiji, Dadu, Sehwan, Johi, Sukkur, Nawabshah, Hyderabad, Karachi, Thar were highly affected by water pollution in different aspects.

While studying total arsenic, inorganic arsenic species and fluoride ion contaminations in underground water of Diplo and Chachro sub district of Tharparkar, Pakistan were investigated in present study resulting the concentrations of total As, inorganic As species, fluoride ion and others physicochemical parameters were reported in terms of basic statistical parameters, principal component analysis, cluster analysis, sodium absorption ratio and saturation indices [29]. The As (III) was determined by cloud point extraction using ammonium pyrrolidinedithiocarbamate (APDC) as complexing reagent, and complex was extracted by surfactant-rich phases in the non-ionic surfactant Triton X-114; the surfactant-rich phase was diluted with 0.1 mol/L HNO_3 in methanol after centrifugation [24]. While total inorganic arsenic (iAs) was determined by solid phase extraction using titanium dioxide (TiO_2) as an adsorbent, the solid phase was prepared

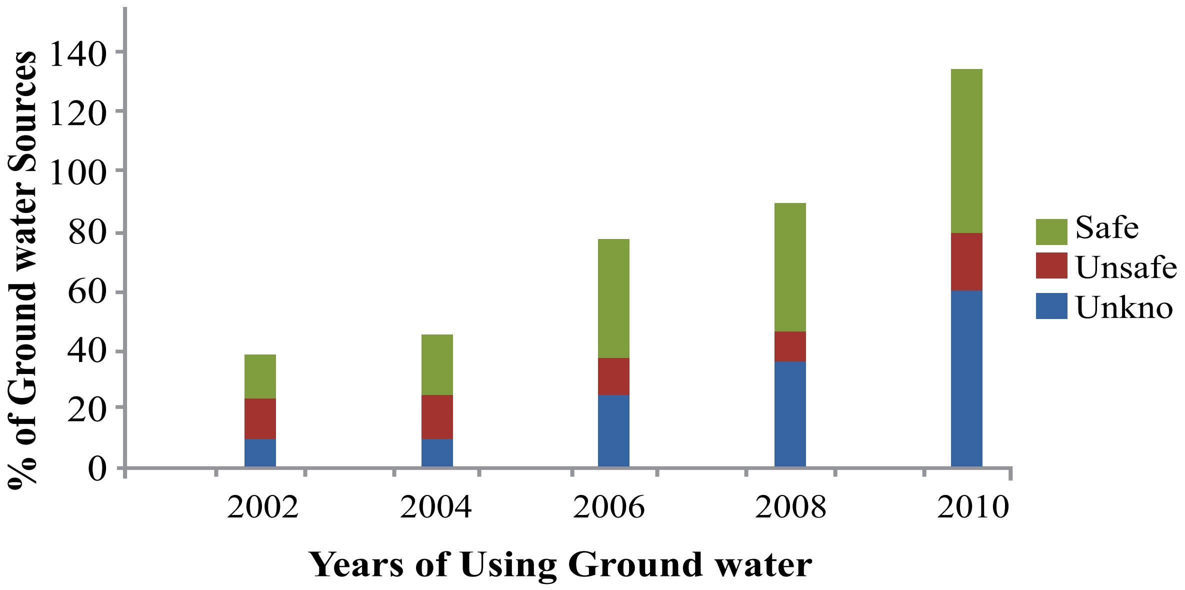

Figure 3: Drinking water condition in Karachi, Sindh Province.

to be slurry for determination after centrifugation. The extracted As species were determined by electrothermal atomic absorption spectrometry. The positive correlation (r=0.640, p=0.671) was observed between total As and it species with F^-. The results showed that underground water samples in the two areas in Tharparkar were severely contaminated with arsenic and fluoride ion, which are exceeded the World Health Organization (WHO) provisional guideline value, and according to United States Environmental Protection Agency, the maximum contaminant level was 0.01 mg/L and 1.5 mg/L, respectively. In the current studies, the chemistry of fresh and stored rainwater of Thar Desert, Pakistan, was estimated during two consecutive monsoon periods, contaminated water was reported [24].

Drinking water condition is worst crossing WHO guideline in Karachi city in Sind province, previous results showed that less than 40% of drinking water comes from groundwater is safe, other is either unsafe or unknown, this survey was done in 2014 [24]. It is estimated that the situation will be worse than the Figure 3. In July 2017, a report showed that 91% of water in Karachi unfits for drinking, because of facing with leaky pipes, faulty treatment plants and illegal tapping, the government of Sindh struggled to provide clean and safe water to Karachi's galloping population [30]. In all, 118 drinking water samples were collected from Karachi: 99 from surface water sources like supply systems, filtration plants and pumping stations; 13 from underground water sources; 3 from reverse osmosis (RO) plants and 3 from other ground and surface water sources (the third pole 2017). Based on physiochemical analysis, 21 (17.8%) water samples were found unsafe for drinking due to turbidity (cloudiness) values beyond the safe limits. From the bacteriological stand point, 104 (88.1%) were found to have coliform bacteria beyond the World Health Organisation values (0/100 ml cfu) and 40 (33.4%) had faecal contamination (presence of E. coli). The overall data showed that 107 (90.7%) samples collected from various places in Karachi were unsafe for drinking [30].

Aqueous Arsenic Contamination in Punjab province

In Punjab, Pakistan Environmental Protection Agency reported that arsenic in ambient air particulate matter in the Lahore district varies from of 230 to 2230 ng/m^3, which was much higher than those reported in other areas in the world, for example, 91-512 ng/m^3 in Calcutta, India, 25 ng/m^3 in Wuhan City, China, and 1.2-44 ng/m^3 in Los Angles, USA. About arsenic contamination in Punjab, government started a 'clean water project' aimed to address this problem as well. "Districts like Lahore, Kasur, Bahawalpur, Sahiwal, Rahim Yar Khan and Muzaffargarh, situated along the river course, with high arsenic water contamination [31,32]. The Pakistan Council for Research and Water Resources (PCRWR) and UNICEF have undertaken the assessment of drinking water quality since 1999 following the As crisis in Pakistan and other neighbor countries. Consequently, the presence of As contaminated ground waters (10-200 µg/L) has been recognized in many areas of Pakistan, especially in Punjab [33].

Punjab province, both the water sources from depths of less than 100 feet and above 100 feet have arsenic contamination problems. In addition, data analysis gathered by UNICEF, for 6 wells 3 shallow and 3 deep in Muzaffargarh, Punjab province located at lateral distance of 65 feet to 165 feet apart from each other revealed that arsenic in shallow well 20 to 35 feet deep ranged from 2.2 ug/L to 9 ug/L while in deep wells 100 to 350 feet deep, it was from 61 to 170 ug/L the results suggesting that the increase of arsenic with depth in this specific locality.

This seems to show a different pattern from that found in Sindh, where no contamination was found at depth above 150 feet. Hydrogeological investigation details were required to explain such differences. However, one cannot generalize presence or absence of arsenic for given water sources without testing and thus each source has to be tested for arsenic presence before establishing whether it is safe or not (UNICEF). Pakistan Council of Research in Water Resources (PCRWR) reported that Arsenic problem is not as high as highlighted

Pakistan's Province Viz Arsenic Level					
S. No.	**Location**	**No. of Samples in Lab**	**Arsenic>50 ug/L (%age)**	**Arsenic>10 ug/L (%age)**	**Reference**
1	Sindh province	193	10	26	[12,19,20,26,33,34]
2	Punjab province	428	9	36	
3	Balochistan province	71	0	1.4	
4	KPK province	156	0.6	22	

Table 1a: Arsenic contamination level in Pakistan's Province, Pakistan.

Sindh Province						
S. No.	**Location**		**No. of Samples in Lab**	**Arsenic>50 ug/L (%age)**	**Arsenic>10 ug/L (%age)**	**Reference**
1	Khairpur	**Sindh province**	420	1.9	13.6	[12,19,20,34,25,26]
2	Gambat		388	26.3	54.4	
3	Kotdiji		307	0.7	3	
4	Dadu		595	27	59	
5	Sehwan		139	28	44	
6	Johi		140	3	23	
7	Sukkur		12		8	

Table 1b: Arsenic contamination level in Sindh Province, Pakistan.

Coastal Areas Location						
S. No.	**Location**		**Number of Samples**	**Arsenic ug/L**	**TDS**	**Reference**
1	Ibrahim Hydri	Coastal Areas Location	12	8	1259	[12,20]
2	Rahri		10	3.04	1008	
3	Chashma Goth		10	6.56	680	
4	Mubarak Goth		10	5.56	1442	
5	Fagheer Muhammad Goth		10	BDL	2616	
6	Gul Hassan Goth		8	5.36	4192	

Table 1c: Arsenic contamination level in Coastal areas location, Pakistan.

S. No.	**Location**		**Number of Samples**	**Arsenic ug/L**	**Reference**
1	Gujrat	**Site 1**	3	111	[12,19,31]
2	Jhelum		3	70	
3	Sarghoda		3	136	
4	Bahawalpur	**Punjab Province**	25	88	[12,20,33,34]
5	Gujranwala		14	64	
6	Kasur		10	100	
7	Lahore		16	100	
8	Multan		16	94	
9	Shekupura		11	73	
10	Sialkot		10	20	
S. No.	**Location**		**Number of Samples**	**As range**	**Reference**
1	R. Y. Khan	**Punjab Province**	580	3-103	[12,19,35]
2	D. G. Khan		304	May-83	
3	Jhang		595	0-48	
4	Leiah		198	Apr-62	
5	Mianwali		301	0-37	
6	Muzaffargarh		398	Feb-45	
7	Rajanpur		172	Apr-39	
8	T. T. Singh		388	Feb-30	

Table 1d: Arsenic contamination level in Punjab Province, Pakistan.

because sampling way was not proper. There is no doubt that there are many areas in both Punjab and Sindh with high levels of arsenic contamination. Naturally results would show high levels of arsenic contamination in the particular areas if the study has focused on the affected areas [20,30]. Many studies have been done in Sind and Punjab provinces, the results are given in Tables 1a-1d.

Recent studies of agriculture in Pakistan found that arsenic was present in vegetables, that was because Pakistani people use the ground water for crops and also pesticides have produced arsenic in vegetables, although in low concentration but it can increase in the future. This data was taken from Quetta city in Pakistan [17]. Sometimes toxic ions can remain in soil and eventually later found in the food chain and these metals cause health problems in plants and animals through ingestion and drinking contaminated water [34-36].

Recent studies showed that metals can enter food chain through vegetables specially because of irrigating contaminated water and

Sample Type	Location	As (mg/kg) Range Mean	Reference
Okra	Faiz Ganj, Punjab, Pakistan	0.2	[17,26,20]
Sponge gourd		0.36	
Brinjal		0.17	
Battle gourd		0.275	
Bottle gourd		0.39	
Cluster beans		0.603	
Spinach		0.28	
Peppermint		1.01	
Indian Squash		0.804	
Peas		0.63	
Okra	Thari Mir Wah, Sindh, Pakistan	0.8	
Sponge gourd		0.504	
Brinjal		0.39	
Battle gourd		0.811	
Bottle gourd		1.05	
Cluster beans		0.734	
Spinach		0.9	
Peppermint		1.2	
Indian Squash		1.3	
Peas	Gambat, Sindh, Pakistan	0.91	
Okra		0.89	
Sponge gourd		0.612	
Brinjal		0.57	
Battle gourd		1.11	
Bottle gourd		1.25	
Cluster beans		1.3	
Spinach		1.1	
Peppermint		1.7	
Indian Squash		1.63	
Peas		1.03	

Table 2: Arsenic in vegetables in three different cities in Pakistan.

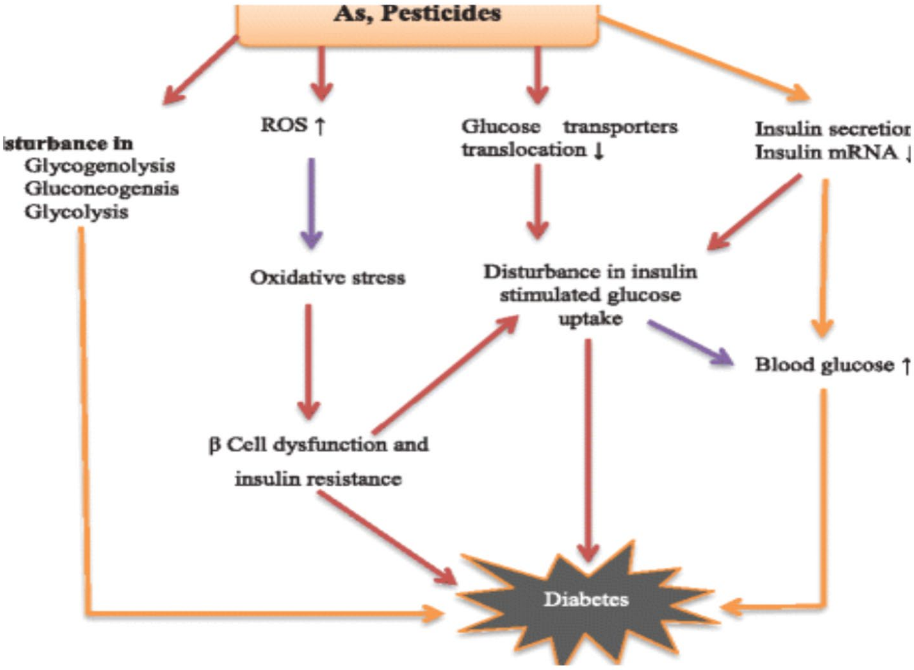

Figure 4: Effect of arsenic and pesticides on health.

pesticides, and then they bring arsenic in food chain. The plants can accumulate extremely large amounts of arsenic while it also depends on the source of pollution and the location [17]. It is proved by agricultural professionals that the use of irrigation water contains arsenic can heavily affect the plant height and the development and growth of roots. Arsenic has been found in spinach, coriander and mint leaves ranging of 0.90-1.20 mg/kg in Southeast Sindh, while the lower arsenic has been detected in the onion, carrot, potato ranging of 0.048 to 0.256 mg/kg [12,27].

Several studies on the linear relationship between arsenic content of vegetation and soil concentrations have been conducted, vegetables samples were taken and found to have arsenic as seen in Table 2 below. Irrigation with arsenic-laden groundwater in Asia also causes bioaccumulation of arsenic [37].

It was reported that total arsenic composite food in daily dietary intake by adults is higher than in other countries, 34.1 g (adult females) and 59.2 g (adult males) in Canada [23]. Irrigation is needed to be systematic while avoiding to provide contaminated water minimize the accumulation of arsenic in plants is needed which was consumed directly by humans, farm animals and wildlife [38-41]. Arsenic is a toxic but organic As compounds such as mono- and dimethylarsinic acids are possibly carcinogenic to humans and are classified as Group 2B by International Agency for Research on Cancer (Figure 4) [20].

In Pakistan, five cities are highly contaminated by arsenic (more than 50 ug/L), namely Lahore, Sheikhupura, Multan, BahalwalPur and Hyderabad [42,43]. Medical researches proved several cases related to arsenic contamination in drinking water that caused Diabetes. Disease caused by drinking water has been found in southern Sindh and Khairpur, several cases have been diagnosed and found to be due to Arsenic presence in drinking water. Arsenic exposure can cause elevated risk for cancers development, such as most notably skin cancer and cancers of the liver [24], lung, bladder, and possibly the kidney and colon [27].

Conclusion

The following major conclusions can be drawn:

Alarmingly high levels of arsenic in ground and surface water in Pakistan have been found because of the rise in arsenic pollution in the past decade when industrialization and urbanization was mainly increasing. Arsenic issues were only found in Sindh and Punjab provinces in Pakistan, where water is contaminated above the WHO level, detailed studies should be conducted around these provinces. According to the studies conducted, both shallow and deep water sources are contaminated. Arsenicosis and some serious issues have been found, details of the data were given by medical departments and therefore detailed survey should be taken under good team. Arsenic has be detected in vegetables because soil and water for irrigation has As contamination

Recommendation

Arsenic and other heavy metal testing facilities should be available at an affordable cost. Easy and sustainable surface water treatment way should be introduced to the public, specially the affected areas. Alternative water supply options should be introduced keeping in view social, cultural and economic status of population. Arsenic is now entering in the ecosystem due to the increased industries; proper remediation strategies must be adopted to minimize the risk to ecosystem. Arsenic issues were only found in Sindh and Punjab provinces In Pakistan, where water is contaminated above the WHO level, so detailed studies should be conducted in these provinces.

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