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Assessment of Arsenic Contamination in Groundwater and Associated Human Health Risk

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Abstract: Drinking water contamination by arsenic (As) is of significant concern due to its potential cause of cancer and arsenicosis. In this study, out of the 200 samples (n = 200), the mean As concentrations ranged from below detection limit (BDL) to 3.30, 4.81, 4.42 and 3.85 µg L^{-1} in small residential, roadside, industrial and household areas, respectively. From 200 total samples, 9% of the groundwater samples showed As levels higher than the WHO safe guideline limit of 10 µg L^{-1}. Human health risk was assessed using average daily intake (ADD), hazard quotient (HQ) and cancer risk (CR) values which were found to be greater than the recommended values by the United States Environmental Protection Agency (1.0 and 10^{-6}) for health risk assessment. The CR were ranged from 0–5.7 × 10^{-1}, 4.0 × 10^{-1}, 2.0 × 10^{-1} and 1.0 × 10^{-1} in small residential areas for children, adolescents, males and females, respectively. In roadside areas, the values ranged from 0–2.8 × 10^{-1}, 4.0 × 10^{-1}, 2.0 × 10^{-1} and 2.8 × 10^{-1} for children, adolescents, males and females, while 0–5.9 × 10^{-1}, 4.1 × 10^{-1}, 2.1 × 10^{-1} and 1.6 × 10^{-1} in industrial areas and 0–8.0 × 10^{-1}, 2.91 × 10^{-1}, 2.6 × 10^{-1} and 3.9 × 10^{-1} were calculated in household sites. All the CR values were found to be exceeding the US-EPA limit (10^{-6}) recommending that the people in the study area are more prone to carcinogenic risk. Overall, it was concluded that due to presence of As in drinking water, these areas tend to be at higher cancer risks. To provide safe drinking water for the people living in these As-affected areas, urgent remedial and management steps are required.

Keywords: contamination; ground water; health; water quality

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Citation: Riaz, R.M.Y.; Murtaza, G.; Farooqi, Z.U.R.; Ali, S.; Aziz, H.; Mahboob, S.; Al-Ghanim, K.A.; Owens, G.; Ahmad, H.R.; Riaz, U. Assessment of Arsenic Contamination in Groundwater and Associated Human Health Risk. *Sustainability* **2022**, *14*, 12460. https://doi.org/10.3390/su141912460

Academic Editors: Stefanos Vrochidis, Demetrios Eliades, Ioannis Papoutsis and Ilias Gialampoukidis

Received: 31 May 2022
Accepted: 23 September 2022
Published: 30 September 2022

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1. Introduction

Water plays a significant role in the biosphere, where it supports all living organisms [1]. However, its contamination with different contaminants deteriorates its quality and makes it unsuitable for consumption, i.e., arsenic (As) contamination of groundwater in the world, especially throughout Southeast Asia is steadily increasing [2,3]. This is an alarming concern, because elevated levels of As in human body can cause long-term detrimental health impacts, i.e., disturbance of the digestive system, reduced synthesis of red and white blood cells, muscle fatigue, skin irritations, malignant skin growth, liver, lung and bladder cancers, cardiovascular and neurological diseases [4]. Thus, the World Health Organization (WHO) has set a maximum allowable As concentration in drinking water of 10 µg L^{-1} [5]; where, due to the high toxicity of As, worldwide concern exists for the high or delayed doses of As in drinking water [6].

Arsenic contamination of groundwater has resulted in a massive epidemic of As related toxicities in several countries, especially in developing countries including Bangladesh [7,8], Cambodia [9], China [10], India [11], Taiwan [12] and Vietnam [13]. It was estimated that approximately 57 million people drink As-contaminated groundwater with concentrations exceeding the drinking water standard recommended by the WHO [14].

Groundwater quality issues are increasing globally due to increasing population and associated industrialization which increases the demand on existing finite shallow groundwater resources [15]. Rapid metropolitan development in cities has additionally placed pressure on groundwater quality due to over exploitation of the natural resource and increases in pollution. Hence, there is an urgent need to monitor and protect groundwater quality as well as remediation [16]. There are numerous remedial techniques being used for As-contaminated water, i.e., adsorption, reduction into less toxic forma and sequestration in plant biomass [17,18]. In Pakistan, groundwater is the main source of drinking water, but this source contains many pathogens including numerous bacterial, viral and primary agents that cause 2.5 million deaths per year from endemic diarrheal diseases. Usage of such low-quality water allows waterborne diseases to spread. In Pakistan, community health studies indicate that 40–50% of all deaths are due to the poor quality of drinking water [19]. As-contaminated groundwater is derived naturally from As-rich aquifer sediments, where the geochemistry of As can be rather complex [20]. Various hydrogeological and biogeochemical factors affect the As concentration in groundwater, such as sediment mineralogy, microbial oxidation or reduction of As, groundwater recharge, groundwater flow paths [21,22] and the presence of fractures in bedrock formations [23].

In Bangladesh, arsenic contamination of tube well waters, which serves as the primary source of drinking water, has long been recognized as a serious public health issue [24,25]. For example, in the Punjab province of Pakistan over 20% of the total population are exposed to As pollution and there are many areas, i.e., Muzaffargarh [26], Rahim Yar Khan [27,28], Vehari [29], Mailsi [30], Bahawalpur [31], Lahore and adjacent areas [32] and Multan [33] in both the lower and upper Punjab, where As is much higher than the recommended WHO value [34]. Since the extent of this As-contamination issue is likely to extend well beyond the boundaries of the Punjab, there is an urgent need to analyze As concentrations in adjacent areas and assess the consequential possible human health risks. Thus, this study is the first step in a planned investigation of As concentrations in groundwater of the Lodhran District, Punjab, Pakistan, and the human health risks associated with intake of As-contaminated water.

2. Materials and Methods

2.1. Description of the Area

The Lodhran District (29.6869 N; 71.6673 E) is situated on the northern side of the Sutlej River in the Punjab, Pakistan and has an agricultural focused economy. The district has total geographical area of 1790 km^2, with a population of around 1.7 million including 1 million people living in urban areas. It is surrounded by the districts of Bahawalpur, Khanewal, Multan and Vehari.

2.2. Groundwater Sampling

Groundwater samples (n = 200) were collected in triplicates from hand and electric pumps installed at varying depths ranging from 30–88 m during summer (June–July), 2019 (Figure 1). The sampling area was divided into four sub-categories, i.e., small residential areas (area with less house and population), households (densely populated area), industrial and roadside areas. Air-tight polythene bottles (250 mL) were used for sample collection. Pumps were kept flowing for 5 min before sample collection to obtain a fresh and representative groundwater sample.

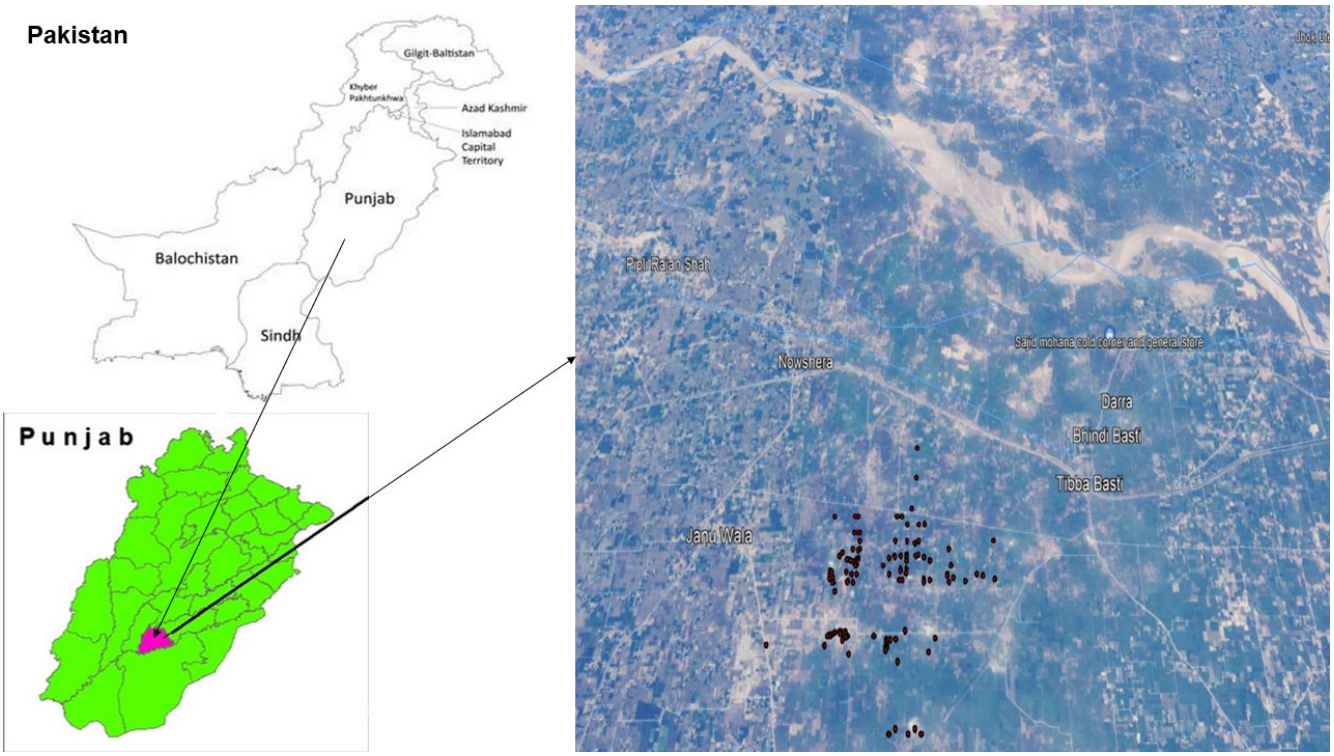


Figure 1. Base map of sampling sites in Lodhran District of Punjab Province, Pakistan.

2.3. Sample Preservation and Quality Assurance

Conductivity, total dissolved solids (TDS) and pH were determined directly on site without any pre-treatment using portable EC (Lovibond SensoDirect con200) and pH meters (Hanna HI-83141) after their calibration as described by Eaton and Franson [35]. After this, two identical sets of samples were collected for anions and metals determination. One set was used for cation and anions determination, while the other was immediately preserved for metals analysis by adding 2–3 drops of concentrated nitric acid (HNO_3) to dissolve metal ions and reduce their precipitation. All collected samples were stored in an insulated cooler containing ice at 4 °C and transported to the Soil and Water Testing Laboratory for Research, Bahawalpur, Pakistan.

2.4. Analytical Procedures

Water samples were analyzed for both physical (color, odor, taste and turbidity) and chemical parameters (Fe and As) using standard methods described by Eaton and Franson [35].

2.5. Metal's Analysis

The iron (Fe) content of collected water samples was determined using atomic absorption spectrophotometer (AAS) (Solaar S-100, CiSA) via a standard procedure by Eaton and Franson [35], while As was also determined using AAS (Solaar S-100, CiSA) equipped with vapor generation assembly (Varian VGA 77) using the method described by Behari and Prakash [36].

2.6. Human Health Risk Assessment

The United States Environmental Protection Agency's (US-EPA) human health risk assessment model Equations (1)–(3) were applied to calculate human health risk associated with consumption of As-contaminated water. This approach allows for individual human

health risk assessment via initial calculation of the average daily dose (ADD) of As due to ingestion of As-contaminated drinking via Equation (1):

$$Average\ daily\ dose\ (ADD) = \frac{ED \times C \times IR \times EF}{AT \times BW} \quad (1)$$

where;

ED = exposure duration (assumed to be 10 and 18 for children and adolescent, respectively, and 67 years each for male and female, which is comparable with earlier studies from Pakistan and other countries),
C = arsenic concentration in water (μg L^{-1}),
IR = ingestion rate of water (L day^{-1}),
EF = exposure frequency (365 days $year^{-1}$),
AT = average lifetime (24,495 days) and
BW = body weight (13 for children, 28 for adolescents, 72 for male and 53 for female in kgs) [37].

Non-cancer risk

The hazard quotient (HQ) was subsequently calculated using Equation (2)

$$Hazard\ quotient = \frac{ADD}{RfD} \quad (2)$$

where RfD is the oral reference dose, equivalent to 0.0003 mg kg^{-1} day^{-1} for As, calculated by the [37]. The health risk was considered elevated when HQ > 1.

Cancer Risk

The cancer risk (CR) was also calculated using the following equation;

$$Cancer\ risk = \frac{ADD}{CSF} \quad (3)$$

where the cancer slope factor (CSF) for As was taken to be 1.5 per mg kg^{-1} day^{-1} according to US-EPA [37]. The parameters used in the health risk assessment are presented in Table 1.

Table 1. Parameters used for health risk assessment calculation.

Age Group	IR (L/Day)	BW (kg)	EF (Days)	ED (Years)	AT (Days)
Children	1	13	365	10	3650
Adolescents	1.5	28	365	18	6570
Adult male	2	72	365	67	24,455
Adult female	2	53	365	67	24,455

2.7. Statistical Analysis

All data obtained were statistically analyzed for mean, minimum, maximum, median and standard deviation using MS Excel (Microsoft corporation, Redmond, Washington, DC, USA) prior to further analysis using either XLSTAT v2018.1 (Addinsoft Inc, New York, NY, USA) and/or Origin 2018b v9.5.1 (OriginLab corporation, Miami, FL, USA).

2.8. Geographic Information System (GIS) Analysis

For the preparation of GIS maps showing As concentration in different areas, GIS software ArcMap 10.2.2 (Esri, Redlands, CA, USA) was used. Inverse distance weightage (IDW) was used to show the As concentration in different study areas.

3. Results

The results from the analysis of 200 groundwater samples from the Lodhran District, including As-concentrations and other common groundwater quality characteristics are summarized via their descriptive statistics in Table 2.

In small residential areas, of the 23 water sample analyzed, 9, 78, 17, 21, 4, 21, 17 and 56% of groundwater samples showed higher As, EC, Fe, Ca, Mg, Cl, hardness and TDS concentrations, respectively, than the safe limits set by WHO, with only pH and turbidity consistently within WHO safe limits (Table 2).

In roadside samples, of the 21 samples analyzed, 10, 61, 5, 43, 9, 19 and 38% of the groundwater samples showed higher As, EC, Fe, Ca, Cl^-, hardness and TDS, respectively, than the safe limits set by WHO, with only pH, Mg and turbidity found within WHO safe limits (Table 2; Figures 2 and 3).

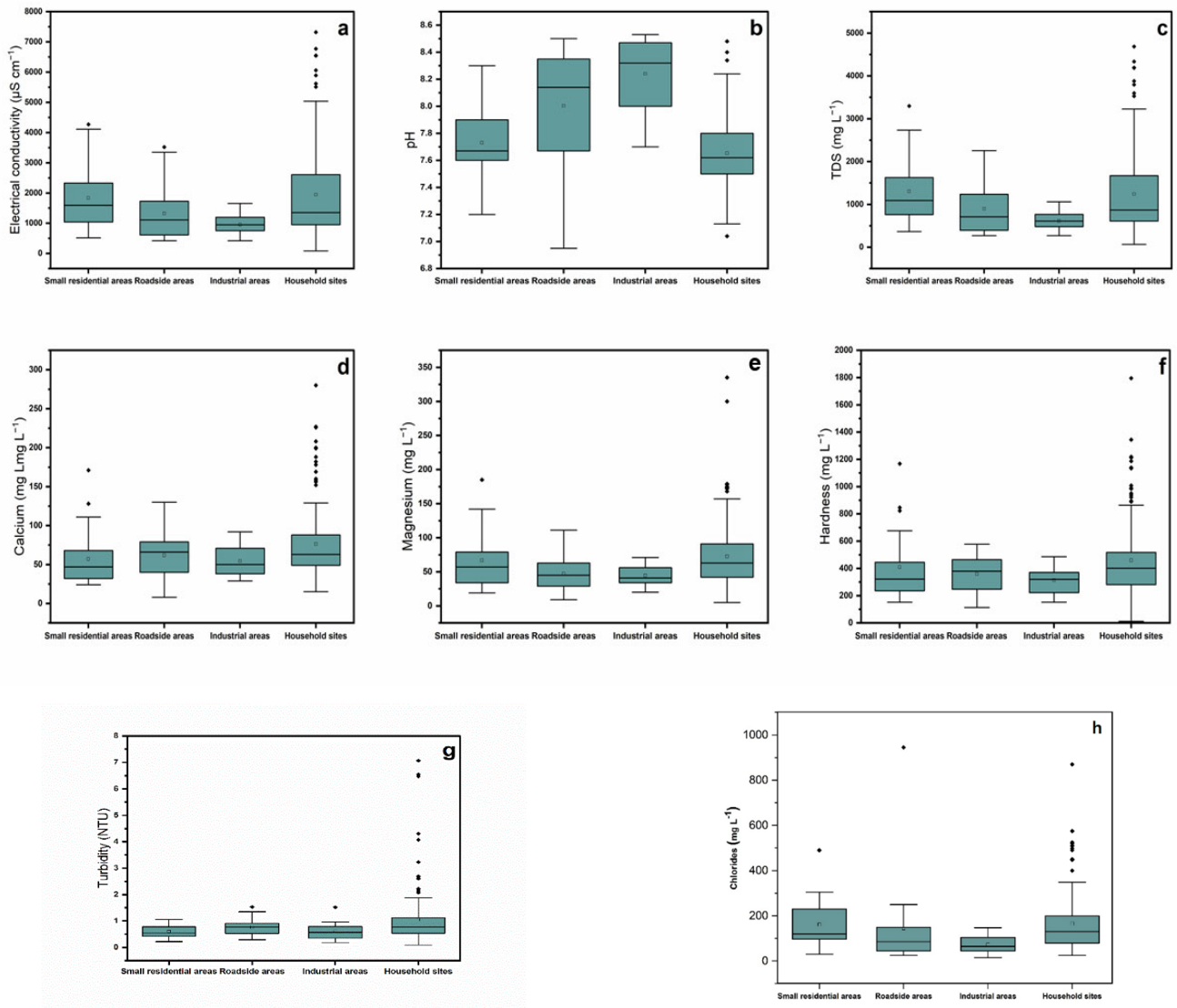


Figure 2. Distribution and variation in (**a**) EC, (**b**) pH, (**c**) TDS, (**d**) Ca, (**e**) Mg, (**f**) hardness, (**g**) turbidity and (**h**) chlorides of the studied area. Group 1 (small residential areas), group 2 (roadside areas), group 3 (industrial areas) and group 4 (household sites). Diamond symbols showing the outliers of the data.

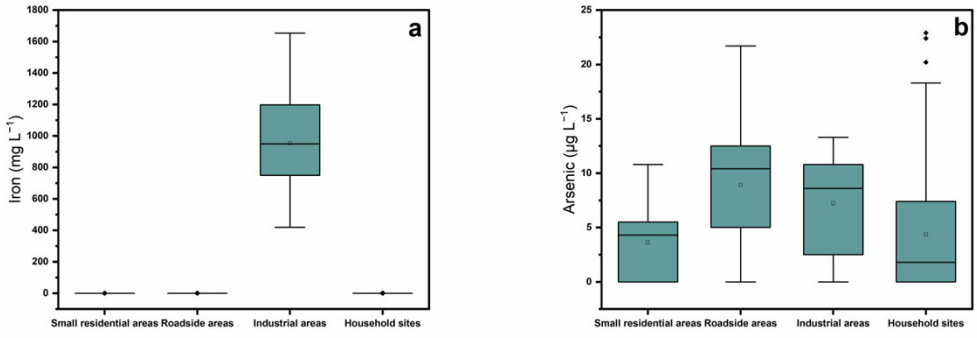


Figure 3. Distribution and variation in (**a**) iron and (**b**) arsenic. Group 1 (small residential areas), group 2 (roadside areas), group 3 (industrial areas) and group 4 (household sites). Diamond symbols showing the outliers of the data.

Of the 15 samples collected from industrial areas, 20, 47, 7, 13, 13 and 7% of the groundwater samples analyzed showed higher concentration of As, EC, Fe, Ca, pH and TDS, respectively, than the WHO safe limits, with only Mg, Cl and turbidity consistently within WHO limits (Table 2). Of the 141 total samples collected from household areas, 8, 72, 11, 35, 15, 27, 42 and 2% of the groundwater samples analyzed showed higher As, EC, Fe, Ca, Cl, hardness, TDS and turbidity, respectively, than the WHO guideline value and only pH consistently remained within the WHO permissible limits (Table 2).

Overall, the results of this study showed that groundwater from the study area was generally detrimentally affected by elevated levels of both major anions and cations as well as high EC as an indicator of salinity. The total hardness of the groundwater samples (Table 2) was generally >180 mg L^{-1} indicating significant groundwater hardness [38,39].

3.1. Correlation between the Studied Parameters

Pearson two-tailed correlation analysis to determine the inter-relationships between the studied parameters showed some significant correlations amongst groundwater quality parameters across the whole study area (Table 3). While As, Cl and Fe were not generally correlated to any of the groundwater parameters studied, pH was significantly but negatively correlated with Mg^+ ($R^2 = -0.954$), hardness ($R^2 = -0.975$) and EC ($R^2 = -0.998$). Other positive significant correlations were found between turbidity and Ca ($R^2 = 0.985$), and EC with TDS ($R^2 = 0.983$), hardness ($R^2 = 0.971$) and Mg^+ ($R^2 = 0.963$).

3.2. Health Risk Assessment of Arsenic

Globally arsenic poisoning due to dietary intake of As polluted water has been well documented [11,27,29]. Here, three health risk assessment parameters (ADD, HQ and CR) for people in Lodhran District exposed to As rich groundwater were calculated as mentioned in the Table 1. These health risk assessment parameters varied with the sampling area. The ADD of As ranged from 0–8.6×10^{-1}, 6.0×10^{-1}, 3.1×10^{-1} and 1.5×10^{-1} in small residential areas for children, adolescents, males and females, respectively. In roadside areas, ADD ranged from 0–4.2×10^{-1}, 6.0×10^{-1}, 3.1×10^{-1} and 4.2×10^{-1}. In industrial areas, ADD ranged from 0–8.8×10^{-1}, 6.1×10^{-1}, 3.2×10^{-1} and 2.5×10^{-1}, while 0–1.2×10^{-0}, 4.3×10^{-1}, 3.3×10^{-1} and 5.9×10^{-1} were recorded in household sites. The highest average HQ value in children was observed at roadside areas whereas the lowest was estimated at small residential areas. Similarly, in male and female, the highest average HQ value was estimated at roadside areas whereas lowest was observed at small residential areas in male and female. The CR were ranged from 0–5.7×10^{-1}, 4.0×10^{-1}, 2.0×10^{-1} and 1.0×10^{-1} in small residential areas for children, adolescents, males and females, respectively. In roadside areas, the values ranged from 0–2.8×10^{-1}, 4.0×10^{-1}, 2.0×10^{-1} and 2.8×10^{-1} for children, adolescents, males and females, while 0–5.9×10^{-1}, 4.1×10^{-1}, 2.1×10^{-1} and 1.6×10^{-1} in industrial areas and 0–8.0×10^{-1}, 2.91×10^{-1}, 2.6×10^{-1} and 3.9×10^{-1} were calculated in household sites (Table 4).

Table 2. Summary statistics for physicochemical water quality parameters in groundwater samples from four different areas.

Parameter	WHO	Small Residential (n = 23)			Roadside (n = 21)			Industrial Areas (n = 15)			Household Areas (n = 141)		
		Med	Range	Mean ± SD	Med	Range	Mean ± SD	Med	Range	Mean ± SD	Med	Range	Mean ±SD
As (μg L^{-1})	10	1.96	0–11.23	3.30 ± 3.20	3.97	0–11.21	4.81 ± 3.97	3.96	0–11.54	4.42 ± 3.96	2.11	0–14.33	3.85 ± 2.10
EC (μS cm^{-1})	1000	1227	81–7320	1791 ± 1096	1110	421–3520	1326 ± 891	950	420–1654	954 ± 328	1351	81–7320	194 ± 14.94
pH (unitless)	6.5–8.5	7.67	6.95–8.50	7.74 ± 0.28	8.14	6.95–8.50	8.00 ± 0.43	8.32	7.7–8.5	8.24 ± 0.22	7.62	7.04–8.48	7.65 ± 0.24
Fe (mg L^{-1})	0.30	ND	0–2	0.12 ± 0.19	ND	0–0.99	0.06 ± 0.21	ND	0–0.99	0.08 ± 0.002	ND	0–2	0.13 ± 0.37
Ca (mg L^{-1})	75	56	8–280	70.9 ± 36.6	66	8–130	61.8 ± 30.2	50	29–92	54.2 ± 18.9	63	15–280	76.2 ± 48.1
Mg (mg L^{-1})	150	55.5	335	67.2 ± 41.8	45	9–111	47.0 ± 23.7	41	20–71	44.5 ± 15.9	63	5–3365	72.6 ± 49.7
Cl (mg L^{-1})	<250	118	15–945	156 ± 102	85	25–945	144 ± 195	65	15–148	72.5 ± 35.9	130	25–870	166 ± 129
Hardness as $CaCO_3$ (mg L^{-1})	500	373	12–1795	432 ± 248	379	114–578	358 ± 132	320	152–486	313 ± 102	401	12–1795	460 ± 285
Turbidity (NTU)	<5	0.75	0.09–7.07	0.93 ± 0.22	0.77	0.29–1.53	0.76 ± 0.33	0.57	0.19–1.52	0.62 ± 0.34	0.77	0.09–7.07	1.03 ± 1.0
TDS (mg L^{-1})	1000	798	63–4685	1162 ± 804	710	269–2253	896 ± 606	608	269–1059	611 ± 210	865	63–4685	1239 ± 962

WHO = Word Health Organization guideline value; Med = median; ND = not detected.

Table 3. Pearson correlation (2-tailed) between studied parameters.

	pH	Turbidity	TDS	Ca^{2+}	Mg^{2+}	Hardness	Cl^{-}	Fe	EC	As
pH	1									
Turbidity	−0.548 (0.451)	1								
TDS	−0.979 (0.020)	0.371 (0.628)	1							
Ca^{2+}	−0.682 (0.317)	0.985 (**0.014**) *	0.523 (0.476)	1						
Mg^{2+}	−0.954 (**0.045**) *	0.532 (0.467)	0.924 (0.075)	0.662 (0.337)	1					
Hardness	−0.975 (**0.024**) *	0.703 (0.296)	0.912 (0.087)	0.813 (0.186)	0.960 (**0.039**) *	1				
Cl^{-}	−0.931 (0.068)	0.502 (0.497)	0.925 (0.074)	0.624 (0.375)	0.780 (0.219)	0.872 (0.127)	1			
Fe^{+}	−0.629 (0.370)	0.870 (0.129)	0.478 (0.521)	0.893 (0.106)	0.743 (0.256)	0.782 (0.217)	0.413 (0.586)	1		
EC	−0.998 (**0.001**) *	0.523 (0.476)	0.983 (**0.016**) *	0.660 (0.339)	0.963 (**0.036**) *	0.971 (**0.028**) *	0.918 (0.081)	0.625 (0.374)	1	
As	0.767 (0.232)	−0.165 (0.834)	−0.796 (0.203)	−0.306 (0.693)	−0.897 (0.102)	−0.739 (0.260)	−0.513 (0.486)	−0.548 (0.451)	−0.794 (0.205)	1

*: Correlation is significant at the $p < 0.05$; values in parenthesis show level of significance (p value).

Table 4. Health risk assessment of study areas.

Area	Gender	ADD (mg kg^{-1} day^{-1})				HQ				CR			
		Mean	Median	Range	SD	Mean	Median	Range	SD	Mean	Median	Range	SD
Small residential areas (n = 23)	Children	2.4×10^{-1}	1.5×10^{-1}	$0–8.6 \times 10^{-1}$	0.24	811.65	502.82	0–2879.48	822.14	1.6×10^{-1}	1.0×10^{-1}	$0–5.7 \times 10^{-1}$	0.16
	Adolescents	1.7×10^{-1}	1.0×10^{-1}	$0–6.0 \times 10^{-1}$	0.17	589.83	350.17	0–2005.35	572.56	1.1×10^{-1}	7.0×10^{-2}	$0–4.0 \times 10^{-1}$	0.11
	Male	9.1×10^{-2}	5.4×10^{-2}	$0–3.1 \times 10^{-1}$	0.08	305.84	181.57	0–1039.81	296.88	6.1×10^{-2}	3.6×10^{-2}	$0–2.0 \times 10^{-1}$	0.05
	Female	5.0×10^{-2}	6.0×10^{-2}	$0–1.5 \times 10^{-1}$	0.05	169.57	200.12	0–502.64	185.78	3.0×10^{-1}	4.0×10^{-2}	$0–1.0 \times 10^{-1}$	0.04
Roadside areas (n = 21)	Children	3.7×10^{-1}	3.0×10^{-1}	$0–4.2 \times 10^{-1}$	2.18	1234.21	1018.92	0–1423.07	729.82	2.4×10^{-1}	2.0×10^{-1}	$0–2.8 \times 10^{-1}$	0.14
	Adolescents	2.5×10^{-1}	2.1×10^{-1}	$0–6.0 \times 10^{-1}$	0.15	859.53	709.60	0–2001.78	508.26	1.7×10^{-1}	1.4×10^{-1}	$0–4.0 \times 10^{-1}$	0.10
	Male	1.3×10^{-1}	1.1×10^{-1}	$0–3.1 \times 10^{-1}$	0.07	445.68	367.94	0–1037.96	263.54	8.9×10^{-2}	7.3×10^{-2}	$0–2.0 \times 10^{-1}$	0.05
	Female	1.2×10^{-1}	7.4×10^{-2}	$0–4.2 \times 10^{-1}$	0.12	415.48	246.66	0–1412.57	403.31	8.3×10^{-2}	4.9×10^{-2}	$0–2.8 \times 10^{-1}$	0.08
Industrial areas (n = 15)	Children	3.4×10^{-1}	3.0×10^{-1}	$0–8.8 \times 10^{-1}$	0.26	1134.01	1015.38	0–2958.97	874.52	2.2×10^{-1}	2.0×10^{-1}	$0–5.9 \times 10^{-1}$	0.17
	Adolescents	2.3×10^{-1}	2.1×10^{-1}	$0–6.1 \times 10^{-1}$	0.18	789.76	707.14	0–2060.71	609.04	1.5×10^{-1}	1.4×10^{-1}	$0–4.1 \times 10^{-1}$	0.12
	Male	1.2×10^{-1}	1.1×10^{-1}	$0–3.2 \times 10^{-1}$	0.09	409.50	366.66	0–106,651	315.80	8.0×10^{-2}	7.3×10^{-2}	$0–2.1 \times 10^{-1}$	0.06
	Female	9.0×10^{-2}	8.7×10^{-2}	$0–2.5 \times 10^{-1}$	0.07	323.93	290.04	0–845.24	249.81	6.4×10^{-2}	5.0×10^{-2}	$0–1.6 \times 10^{-1}$	0.04
Household sites (n = 141)	Children	3.0×10^{-1}	2.8×10^{-1}	$0–1.2 \times 10^{0}$	0.25	1028.33	935.89	0–4041.02	865.06	2.0×10^{-1}	1.8×10^{-1}	$0–8.0 \times 10^{-1}$	0.17
	Adolescents	1.1×10^{-1}	1.0×10^{-1}	$0–4.3 \times 10^{-1}$	0.09	371.34	337.96	0–1459.25	312.38	7.4×10^{-2}	6.7×10^{-2}	$0–2.91 \times 10^{-1}$	0.06
	Male	1.7×10^{-1}	1.1×10^{-1}	$0–3.3 \times 10^{-1}$	0.19	355.94	147.13	0–794.33	880.46	3.3×10^{-2}	1.0×10^{-1}	$0–2.6 \times 10^{-1}$	0.44
	Female	1.5×10^{-1}	1.3×10^{-1}	$0–5.9 \times 10^{-1}$	0.12	504.46	459.11	0–1982.38	424.37	1.0×10^{-1}	9.0×10^{-2}	$0–3.9 \times 10^{-1}$	0.08
Safety limits [37]		5×10^{-8}				1×10^{-4}				10^{-6}			

4. Discussion

4.1. Physico-Chemical Characteristics of Groundwater

The variations in physico-chemical parameters of the groundwater samples collected from across the Lodhran District, Punjab (Table 2, Figures 2 and 3) showed that the highest EC value (7320 μS cm^{-1}) was observed in both small residential and household areas. Since TDS depends on the concentrations of CO_3^{2-}, HCO_3^-, Cl^-, SO_4^{2-}, NO_3^-, Na^+, K^+, Ca^{2+} and Mg^{2+} [17], it ranged from 63–4650, 269–2253, 269–1059 and 63–4685 mg L^{-1} in small residential, roadside, industrial and household areas, respectively. The highest mean TDS contents in groundwater were found in order of household areas > small residential area > roadside area > industrial area. The highest TDS concentration of 4685 mg L^{-1} was found in small residential and household areas, which was attributed to municipal wastewater leaching to groundwater and the consequential pollution of that groundwater [40–43].

The Ca concentrations in groundwater ranged from 8–280, 8–130, 29–92 and 15–280 mg L^{-1} in small residential, roadside, industrial and household areas, respectively. Likewise, the Mg concentrations ranged from 5–335, 9–111, 20–71 and 5–3365 mg L^{-1}, while Cl- ranged from 15–945, 25–945, 15–148 and 25–870 mg L^{-1} in the same areas. Relatively high Ca, Mg and Cl concentrations (76, 3365 and 945 mg L^{-1}, respectively) were observed in the household and roadside areas, which was attributed to the relatively higher amounts of primary minerals in sand such as feldspars and mica [44–46].

With the exception of household areas, groundwater turbidity was generally <5 NTU, but was highly variable, ranging from 0.09–7.07, and was generally attributed to leaching of wastewater and contamination to groundwater [47]. Groundwater hardness ranged from 12–1795, 114–578, 152–486 and 12–1795 mg L^{-1} as $CaCO_3$ in small residential, roadside, industrial and household areas, respectively. The highest water hardness (1795 mg L^{-1}) was found in both the small residential and household areas, and was, again, attributed to municipal wastewater pollution and higher amounts of primary minerals (quartz, biotite, mica, etc.) [45].

4.2. Metals (As and Fe) Concentration in Groundwater

The maximum concentrations of As in the groundwater were found 11.23, 11.21, 11.54 and 14.33 μg L^{-1} in small residential, roadside, industrial and household sites, compared to the permissible limits of 10 μg L^{-1}, while Fe was found from BDL to 0.72, 0.99, 0.99 and 2.00 mg L^{-1} Fe in small residential, roadside, industrial and household sites. Average concentrations of As varied in the order of roadside areas < small residential areas < industrial areas < household sites. The highest mean value of As was found in roadside areas (4.81 μg L^{-1}). Fe concentrations ranged from BDL-to 0.72, 0.99 and 2.00 μg L^{-1}, in small residential, roadside, industrial and household sites. The average concentrations of Fe varied in the order small residential areas = household areas < industrial areas < roadside areas. The highest mean Fe concentration found in small residential and household areas (0.12 and 0.13 mg L^{-1}, respectively). The standard deviation (SD) indicated high variabilities for both As and Fe. The higher concentrations of groundwater As were attributed to sandy soil types and low rainfalls in the region, so that such soils had higher amounts of dissolved carbon dioxide which promoted dissolution of carbonates and silicates and released the As-associated species into the groundwater [48]. The spatial distribution pattern of As (Figure 3) showed that the higher As concentrations were mainly located in the southern and eastern parts of the study area (i.e., household sites). Moreover, application of As-contained pesticides and geogenic sources are also responsible for alleviated As levels in groundwater [32].

4.3. Health Risk Assessment of As-Contaminated Water Consumption

Across the district the toxic risk index generally decreased in the order of small roadside areas > small residential areas > industrial areas > household areas as the ADD values varied in the same order. Likewise, since HQ was derived from ADD, HQ also changed in the order, i.e., small roadside areas > small residential areas > industrial areas

> household areas. The calculated CR index values also decreased in the same order as in the case of ADD and HQ. Since, CR values > 1 in a million (1×10^{-6}) are considered significant [32]. The results warn that exposure to As in the study area is a moderate human health risk and requires immediate attention of local agencies such as the Water and Sanitation Agency, which are responsible for the proper disposal of wastewater and provision of clean water to residents. Similar results to our study were reported by Zhang et al. [39] in Jinghui region of China with As concentrations of 0.0012 to 0.0190 mg L^{-1} and 2.58% of the collected samples were exceeding the national guideline of 0.01 mg L^{-1}. He also reported the carcinogenic risk up to 3.50×10^{-4} in the study area compared to limit of (1.00×10^{-4}).

5. Conclusions

The present study shows that drinking water quality within the study area was poor and was unfit for drinking when compared to the WHO safe drinking water limits for As, EC, Fe, Ca^{2+}, hardness and TDS. Arsenic levels of up to 14.33 μg L^{-1}, more than double the recommended levels of 10 μg L^{-1} set by WHO were recorded. In fact, out of 200 samples collected, 9% had As concentrations > 10 μg L^{-1}; where, exceedance of guideline values varied with the area studied, being 9% in small residential areas, 10% in roadside areas, 13% in industrial and 8% in household areas. Calculation of all three toxicity indices, indicated that the possibility of human health risks due to ingestion of As-contaminated water was elevated in the area. To reduce human exposure via drinking of As contaminated water, there is an urgent need for As mitigation and awareness program throughout the Lodhran District.

To efficiently achieve this goal, it is recommended that:

- To overcome the groundwater contamination with anion and cations, the outdated sewerage system needs to be renovated/repaired, since seepage of wastewater into the groundwater and consequential contamination is largely attributed to wear and tear of an aged sewage treatment system.
- Water filtration plants at large scales and local scale filtration technologies should be adopted for arsenic and other metals removal from ground/drinking water.
- Proper management of wastewater and solid wastes is necessary to avoid groundwater pollution.
- Water And Sanitation Agencies (WASA) across Pakistan should comply with the WHO standards for drinking water and supply clean drinking water to the areas affected by As pollution.
- WASA should properly monitor the groundwater quality in rural areas to avoid health risks associated with As-contaminated water used for drinking purposes.

Author Contributions: Conceptualization, G.M.; methodology, S.A., H.A. and Z.U.R.F.; software, H.R.A. and U.R.; validation, S.M.; formal analysis, R.M.Y.R., H.A. and K.A.A.-G.; resources, G.M.; data curation, writing—original draft preparation; R.M.Y.R., and Z.U.R.F. writing—review and editing, G.M., G.O., S.M., K.A.A.-G. and H.A.; visualization, H.R.A., S.A. and S.M.; supervision, G.M. and S.A. All authors have read and agreed to the published version of the manuscript.

Funding: Special Thanks to Higher Education Commission (HEC) Pakistan for support.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: All the data are presented in the manuscript.

Acknowledgments: Special thanks to the Institute of Soil and Environmental Sciences, University of Agriculture, Faisalabad, Pakistan, for support. The authors express their sincere appreciation to the Researchers Supporting Project Number (2021/93) King Saud University, Riyadh, Saudi Arabia.

Conflicts of Interest: The authors declare no conflict of interest.

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