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Risk Assessment of Arsenic and Cadmium in Groundwater of Talukas Ghorabari and Mirpur Sakro, Sindh, Pakistan

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Abstract

The current study was carried out for quantitative and risk assessment of cadmium (Cd) and arsenic (As) from Talukas Ghora Bari and Mirpur Sakro. The concentration of Cd was determined using Atomic Absorption Spectroscopy instrument. The As concentration was measured with the help of the Arsenic Kit Method. For analysis of Cd, samples were prepared by the Microwave digestion method, whereas for As analysis, water samples were analyzed directly. The range of Cd content was observed from the studied areas as 1 – 10 µg/L and 1.2 – 11.2 µg/L, respectively. The groundwater water of Talukas Ghorabari and Mirpur Sakro showed the mean Cd content of 5 µg/L and 6.1 µg/L, respectively. The Cd contamination of 56% and 80% was found in Ghorabari and Mirpur Sakro, respectively. The range of As content of 0.00 – 50 µg/L and 10 – 80 µg/L was determined from Ghorabari and Mirpur Sakro, respectively. Hazard Quotient for Cd > 1 was found in 40% of both children and infants in the groundwater of the study area, which may cause non-carcinogenic risk. About 48% of water samples declared HQ values > 1 for adults in the water of Ghorabari. Since 84% of samples showed the HQ values > 1 for children and infants. The HQ values of As for Adults of the Mirpur Sakro were observed in 63.3% samples, whereas for children and infants, HQ values were found in 100% samples. It is therefore strongly recommended that groundwater must be treated before consumption by the people of the area under study.

Keywords: Groundwater, Arsenic, Cadmium, Children, Reverse osmosis, Hazard Quotient

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Introduction

There are various sources of drinking water based on the availability of surface water and groundwater [1]. The severe natural catastrophe and public health hazard arise due to contaminated drinking water, which may initiate from geogenic and anthropogenic sources [2]. The release of industrial wastewater extensively varies the quality of water and contributes to water pollution among the above sources [3, 4]. The potentially toxic elements (PTEs), biological parameters and physic-chemical characteristics are included in water quality parameters because of their toxicity, bio-accumulative, and non-degradable nature. Essential elements such as Zn, Fe, Cr, Cu, Mn and Ni are needed at a particular level for the normal function of living, whereas their large amounts may cause detrimental consequences [5,6]. The minute levels of Hg, As, Cd, and Pb are extremely harmful to life. The detrimental results of these PTEs include carcinogenesis, teratogenesis, heart problem, nerve damages, anaemia, vomiting, abdominal ache and headache [6].

Exposure to high Cd level may cause chronic and acute health hazards accompanied by cancer. Through different ways, people are infected by pathogens present in water. Waterborne diseases are liable to occupy 20 – 30% of beds of hospitals and deaths of infants in Pakistan [1]. About 55% population of Pakistan lives in rural areas of the country with no facility of drinking water quality. Therefore, the residents of villages usually suffer from different diseases like skin problems, food poisoning, kidney problems, stomach problems, and typhoid fever which may be due to sewage water [7]. Thus, a regular focus on water quality was carried out from both developed and developing countries like the USA and Bangladesh. The water pollution dilemma is observed more ferocious in developing countries because of the low investment in treatment service and high development of people. Pakistan, like neighbouring countries, also faces serious water pollution issues in megacities [8]. Therefore, water quality, health hazards, a pattern of water from the area under study has been determined by environmental investigations [9].

It is believed that As is one of the toxic and highly poisonous elements. As is ranked as group 1 human carcinogenic by full name IARC and USEPA [9]. As is also ranked at the top among 20 priority harmful substances by the Agency for toxic substances and disease registry [10]. Reports show that one-third of every 60 living on this planet consumes groundwater with As content above 50 µg/L. There are different sources of As contaminating the environment either natural processes or through anthropogenic activities consisting of the use of fertilizers, pesticides in agriculture, irrigation with arsenic-contaminated water, smelting, mining, and wood preservatives. Earth’s crust contains more than 200 minerals containing As abundance of which 20% is in the form of arsenites, arsenides, silicates, oxides, and elemental As, 20% are sulfides and sulfosalts, and 60% are in arsenate form. As occurs in the environments of soil and water in four oxidation numbers: As (V), As (III), As (0) and As (-III) [11]. Inorganic As is more toxic and mobile than organic As. Arsenite (As(III)) and Arsenate (As(V)) occur in the natural atmosphere and are extremely poisonous and mobile; As(V) is under oxidized environments and As(III) exists in reduced conditions.

Numerous countries of the globe are facing the threat of As contamination of groundwater, including Japan, the United States, Taiwan, Hungary, Canada, New Zealand, Poland, Mexico, Argentina, Chile, Pakistan, China, India and Bangladesh [12-14]. As contaminated groundwater is utilized by various areas of Punjab and Sindh provinces in Pakistan and a large population of Bangladesh as well, and 59 districts of West Bengal in India [15-18]. In some countries, As was observed in groundwater > 3000 µg/L which may be released by geological processes into aquifers. The safe level of As in drinking water as recommended by the WHO is 10 µg/L mostly followed all over the world except some Southeast and South Asian countries [19]. Given the WHO recommendations for As in groundwater, about 200 million people all over the world are at the threat of As contamination and 100 million people are facing As-induced risk in Southeast and South Asia [20,21]. The purpose of this research was to evaluate the potential hazards of Cd and As in groundwater of two Talukas of district Thatta namely Ghorabari and Mirpur Sakro, using Flame Atomic Absorption Spectrometer (FAAS) and

Arsenic Kit Method to measure the health risks associated with Cd and As contamination.

Health Risk of Arsenic and Cadmium

Health impacts of prolonged exposure to As may cause internal cancers (bladder, kidney, lung, and liver), skin cancer, crucial dermatological disorders, along with abdominal, respiratory, neurological, haematological, cardiovascular, obstetric, reproductive illnesses, diabetes, lung's vulnerability, and other As-related diseases [22]. In addition to As, contamination of trace metal pollution is also a serious health concern to residents living in As-contaminated areas [23]. Furthermore, Cd can damage the liver, kidney, and female reproduction system. Therefore, identifying As and other PTEs and their possible contamination sources are the key factors to understanding the groundwater contamination pattern as well as to carrying out the health impact assessment of an area [24].

Materials and Methods

Study Area

Ghorabari and Mirppur Sakro are the study areas situated in coastal areas of district Thatta, Sindh, Pakistan. Coordinates of Ghorabari are 24° 13' 0" N, 67° 34' 0. Its population is about 174,088. Mirpur Sakro is the major town on the route to Karachi. Township of Mirpur Sakro is situated 85 km away from Karachi, while it is 33 km away from Thatta. The coordinates of the study area are 24°33'N 67°38'E24.550°N 67.633°E. The altitude of Mirpur Sakro is about 35 meters, having a population of about 340,834 residing in scattered and towns form and Sindhi is the local language spoken in the area. The important features of this village include Sakro Qabrustan (graveyard) and Gharo–Keti Bandar highway (88 km in length). The land of the villages consists of a large ploughed field. Mirpur Sakro is less developed since roads are unpaved and cob houses made by the residents. Health care centers and personal care clinics are less in the area. It was observed in the present study that people of the study area derived drinking water from hand pumps situated mostly in rural areas of the two Talukas Ghorabari and Mirpur Sakro. Map of the study area is given in Fig. 1.

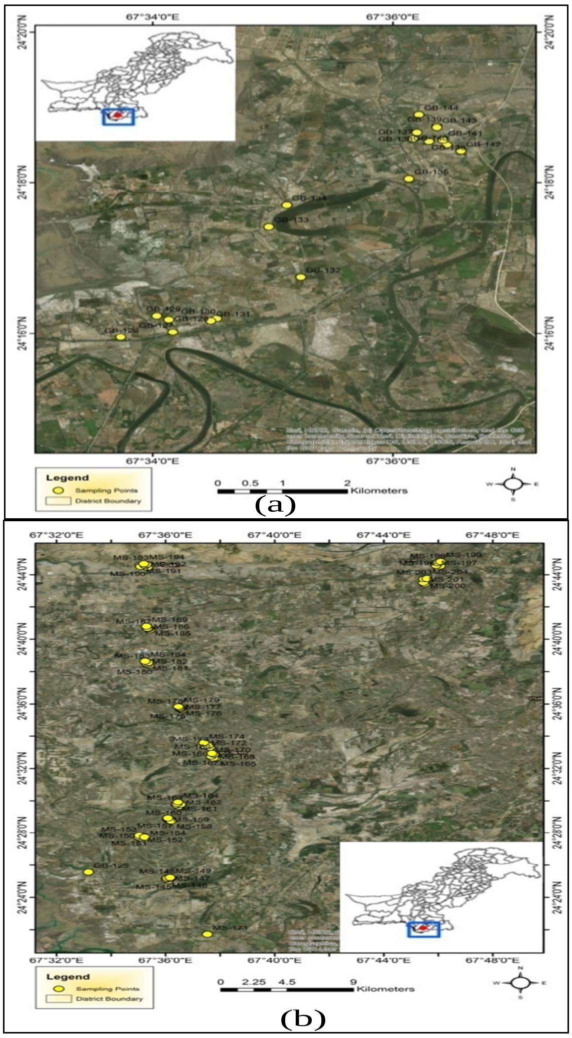

Figure 1. **Map of sampling locations of Talukas Mirpur Sakro and Ghorabari**

Sample Collection

Samples were collected from 55 sampling locations from two Talukas

Ghorabai and Mirpur Sakro. Sampling was done from the groundwater of particularly rural areas situated in mentioned Talukas. From Taluka Ghorabai 25 drinking water samples were collected and 30 water samples were collected from Taluka Mirpur Sakro in polyethylene plastic bottles. Thorough washing of bottles was carried out by double distilled water and detergent. The same sample was used to rinse the bottles three times before filling them with samples. Triplicate samples from each sampling point were collected and covered tightly. Samples collected from Taluka Ghorabari were labelled as G–120 to G–144, while samples taken from Taluka Mirpur Sakro were labelled as M–145 to M–174. Usually, hand pumps were fitted by villagers to get groundwater for drinking, cooking, and washing purposes. Groundwater source was run for 2 – 5 min till fresh water. Samples were acidified with 1 mL of concentrated nitric acid for the preservation purposes. All water samples were transported to Shah Abdul Latif University, Khairpur for preparation and analysis purpose.

Sample Preparation and Analysis

In PTFE flasks 500 mL drinking water samples were taken, then flasks were closed and subjected to microwave irradiation in closed vessel microwave digestion system using Milestone Ethos D model (Sorisole-Bg, Italy). Digestion plan of the microwave oven was pertained at 100 W (2 min), at 250 W (6 min), at 400 W (5 min), at 550 W (8 min) and ventilation for 8 min. The contents of the flasks were cooled and then diluted to 10 mL with (0.2 M) HNO_3. Similarly, reagent blanks were also made by the same procedure. The microwave digestion method has an advantage over the conventional digestion method because it takes less time to digest water samples and it has less chance of evaporation of elements, so more precise extraction of elements from samples than in the conventional method. Also, less acid for digestion for water samples is used [25]. Cd content in drinking water samples was detected using the Analytic Jena model AAS. Finally, the average values of Cd were recorded. The calibration of the Analytic Jena AAS was conducted using a standard solution of Cd to facilitate the calibration graph before Cd measurement and 0.9989 was the correlation coefficient of the standard curve achieved (Fig. 2). As concentration was measured with the help of the Arsenic Kit Method at Pakistan Council of Research in Water Resources (PCRWR) Government of Pakistan, Ministry of Science & Technology Water Quality Laboratory, Nawabshah. Double distilled water and analytical grade reagents were used throughout the present work.

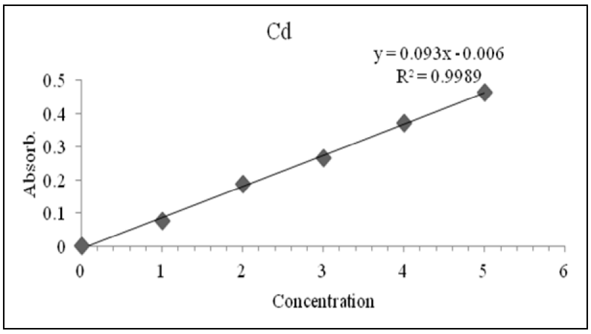

Figure 2. **Calibration curve for the determination of Cd from water samples using AA spectrophotometer**

Health Risk Assessment

The process in which potential health effects of a pollutant on a person from a prescribed amount acquired through one or more ways is known as risk assessment [26]. Health risk assessment for humans is a fruitful technique providing quantitative analysis for environmental monitoring and potential risk supervision of pollutants in various atmospheric means [27]. Since the non-carcinogenic, as well as carcinogenic health risks of Cd in Ghorabari and Mirpur Sakro, District Thatta, through drinking water consumption in adults, children and infants were assessed in current work. The performance of risk assessment of carcinogenic and non-carcinogenic metals in drinking water samples was conducted using USEPA human health risk assessment techniques [28]. It was believed in the present work that the major path of exposure to Cd of residents was the ingestion, while the negligible effect was found through adsorption. The equation (i) was used to calculate the value of mean chronic daily intake (CDI, mg/kg/day) adopted from USEPA [29]:

$$CDI\ ingestion = \frac{Cw \times DI \times F \times EP}{BW \times AT} \quad (1)$$

Where C_W, D_I, F, EP, BW and AT are Cd content (mg/L), mean daily ingestion (L day), exposure frequency (days/years), exposure duration (years), body weight (kg), and average time (days), respectively. For adults, children, and infants, default values for the measurement of chronic daily intake are provided in Table 1. These parameters were adopted from work reported previously [30].

Table 1. **Default values for adults, children and infants for measurement of chronic daily intake for three age groups for Cd and As exposure assessment via drinking water.**

Risk Exposure Factor	Infant	Children	Adult	Unit
CDI	0.8	1.5	2	mg/L/day
F	365	365	365	days/year
EP	1	10	70	years
BW	10	20	70	kg
AT	365	3650	25550	days

However, the human health risk assessment was calculated using As daily intake (ADI) using the equation:

$$ADI = \frac{Cw \times DI}{BW}$$

Where ADI, *Cw*, *BW* are As daily intake, mean concentration of As in groundwater, daily water intake, and mean weight of the body. Daily water intake and the bodyweight of common people were assumed to average 3.0 to 3.5 L, and 65 kg, respectively.

Hazard Quotient (HQ) of Cd was calculated by the ratio of *CDI ingest* to *RfD ingest* through drinking water consumption as [31]:

$$HQingest = \frac{CDIingest}{RfDingest} \quad (2)$$

HQ ingest, *CDI ingest* and *RfD ingest* are the hazard quotient, CDI, and reference dose, respectively. However, the reference dosage may be derived from “No Observed Adverse Effect Level (NOAEL), and explained as upper limit daily allowable dose that permits the exposed people to get this limit of exposure for a large time, excluding the occurrence of any harmful effects. *RfD ingest* level was found from previously reported papers [32]. For the present work, a value of 5.0E −04 mg/kg/day of *RfD ingest* was used for Cd in drinking water. The value of HQ < 1 may not impose adverse effects, while HQ > 1 may cause potential health impacts. Depending on the USEPA, Cd and As are believed to be a human carcinogens and are categorized in group A [33]. Thus, in the present study, the carcinogenic hazard was also measured. For carcinogenic risk, Incremental Lifetime Cancer Risk (ILCR) was utilized. The increment chance of a person growing cancer for the period of lifetime due to contact with a carcinogenic chemical through ingestion is the ILCR. CDI rate multiplied by cancer slope factor (CSF) was used to get carcinogenic health hazards. Equation (iii) was used to calculate the ILCR as [15]:

$$ILCR = CDI \times CSF \quad (3)$$

CSF is used for quantitative contaminant strength and specific for the individual contaminants. The value of 6.1 mg/kg/day was applied to measure cancer risk for the present work [34]. Three subgroups were selected for potential health risk assessment: adults, children, and infants. For estimation of exposure of humans to Cd in water was followed from the USEPA guideline. In the end, all statistical analyses were performed using SPSS software version 18.

Results and Discussion

Cadmium Content in Drinking Water

Commonly, Cd is classified among one of the most ecotoxic metal and shows highly adverse effects on the health of the people. Concerns regarding the adverse impacts of Cd on human health are enhanced because of its atmospheric contamination; particularly, kidneys are vulnerable due to Cd toxicity [27]. From the studied area of Ghorabari and Mirpur Sakro, the range of Cd was observed as 1 – 10 µg/L and 1.2 – 11.2 µg/L, respectively. Since the drinking water showed the mean Cd content of 5 µg/L and 6.1 µg/L in Talukas Ghorabari and Mirpur Sakro, respectively. However, the WHO guideline of Cd is specified as 3 µg/L. As a result Cd contamination of 56% and 80% were found in Ghorabari and Mirpur Sakro, respectively Table 2 and 3.

Table 2. **Cd content, CDI and HQ among three age groups residing in Taluka Ghorabari.**

Sample ID	WHO Limit (3 µg/L)	Adults		Children		Infants	
	Cd (µg/L)	CDI	HQ	CDI	HQ	CDI	HQ
G-120	2	5.71E-05	0.11	0.000150	0.30	0.00016	0.32
G-121	2	5.71E-05	0.11	0.000150	0.30	0.00016	0.32
G-122	7	0.000200	0.40	0.000525	1.05	0.00056	1.12
G-123	5	0.000143	0.29	0.000375	0.75	0.00040	0.80
G-124	9	0.000257	0.51	0.000675	1.35	0.00072	1.44
G-125	9	0.000257	0.51	0.000675	1.35	0.00072	1.44
G-126	6	0.000171	0.34	0.000450	0.90	0.00048	0.96
G-127	5	0.000143	0.29	0.000375	0.75	0.00040	0.80
G-128	10	0.000286	0.57	0.000750	1.50	0.00080	1.60
G-129	7	0.000200	0.40	0.000525	1.05	0.00056	1.12
G-130	3	8.57E-05	0.17	0.000225	0.45	0.00024	0.48
G-131	8	0.000229	0.46	0.000600	1.20	0.00064	1.28
G-132	7	0.000200	0.40	0.000525	1.05	0.00056	1.12
G-133	8	0.000229	0.46	0.000600	1.20	0.00064	1.28
G-134	2	5.71E-05	0.11	0.000150	0.30	0.00016	0.32
G-135	1	2.86E-05	0.06	0.000075	0.15	0.00008	0.16
G-136	3	8.57E-05	0.17	0.000225	0.45	0.00024	0.48
G-137	3	8.57E-05	0.17	0.000225	0.45	0.00024	0.48
G-138	2	5.71E-05	0.11	0.000150	0.30	0.00016	0.32
G-139	8	0.000229	0.46	0.000600	1.20	0.00064	1.28
G-140	1	2.86E-05	0.06	0.000075	0.15	0.00008	0.16
G-142	2	5.71E-05	0.11	0.000150	0.30	0.00016	0.32
G-142	2	5.71E-05	0.11	0.000150	0.30	0.00016	0.32
G-143	6	0.000171	0.34	0.000450	0.90	0.00048	0.96
G-144	7	0.000200	0.40	0.000525	1.05	0.00056	1.12

Table 3. **Descriptive statistics of Cd (µg/L), CDI (mg/kg/day) and HQ (no unit) among three age groups of studied area (Ghorabari and Mirpur Sakro).**

	Taluka Ghorabari								
	Adults			**Children**			**Infants**		
	Maximum	***Minimum***	***Mean***	***Maximum***	***Minimum***	***Mean***	***Maximum***	***Minimum***	***Mean***
Cd (µg/L)	10	1	5	-	-	-	-	-	-
CDI (mg/kg/day)	2.86E-04	2.86E-05	1.43E-04	7.5 E-04	7.5 E-05	3.75E-04	8.0 E-04	8.0 E-05	4.00E-04
HQ	0.57	0.06	0.2848	1.5	0.15	0.75	1.6	0.16	0.8
	Taluka Mirpur Sakro								
	Adults			**Children**			**Infants**		
	Maximum	***Minimum***	***Mean***	***Maximum***	***Minimum***	***Mean***	***Maximum***	***Minimum***	***Mean***
Cd (µg/L)	11.2	1.2	6.1	-	-	-	-	-	-
CDI mg/kg/day	3.20E-04	3.43E-05	1.74E-04	0.00084	0.00009	0.000458	0.000896	0.000096	0.000488
HQ	0.64	0.068571	0.348571	1.68	0.18	0.915	1.792	0.192	0.976

Cadmium in Other Parts of Pakistan

Minimum and maximum Cd concentration of 8.28 – 85.0 µg/L was found in tube well water at Skindar and Latifabad town. About 45% of water samples of Zhob valley, Balochistan, exceeded the WHO limit of 3.0 µg/L of water. The concentration of toxic metals such as Pb, Cu, Cr and Cd was observed within the permissible limit given by the WHO guideline. The literature shows that heavy metals pollution from irrigation with wastewater against groundwater was investigated from District Sahiwal located in the neighbourhood of Lahore. Analysis of vegetables, soil, and irrigated water was conducted for Zn, Mn, Cd, Cu, Pb, Ni, and Fe. The health risk index, daily intake of metals, and metal transfer factors were measured. Surpassed limits of Pb, Mn, and Fe in groundwater-irrigated vegetables, Pb, Cd, Mn, and Fe in wastewater-irrigated vegetables, and Mn, and Cd in wastewater irrigated soil were observed in Spinach and Mustard than WHO specified limit. Exceeded limit of Cd than WHO level was observed in 45% samples in groundwater of Lower Dir, Cd content was observed health risk index > 1 [35]. Results of plant samples, soil samples and wastewater samples collected from three Tehsils of district Vehari. These results indicated the Cd content greater than the permissible limit in wastewater samples of the district Vehari [36]. The maximum PTE pollution was observed in hand pump water samples showed an HQ level of 11.7 for Cd. Greater HQ value than one was found in drinking water sources of the studied area, which may induce different chronic and acute health troubles in people [37].

Arsenic Concentration in Drinking Water

The concentration of As was found greater than the allowable limit of 10 µg/L in 48% samples of Taluka Ghorabari. A maximum and a minimum As level of 0.0 to 50 µg/L and 10 to 80 µg/L were observed in Ghorabari and Mirpur Sakro, respectively (Table 4). The range of ADI was measured as 0.0 to 2.42 µg/kg/day in the groundwater water of the rural area of Ghorabari. The ADI range of the groundwater of Mirpur Sakro was measured as 0.323 to 4.038 µg/kg/day. The results reveal that 63.3% of samples showed the ADI greater than the safe limit in the groundwater of Mirpur Sakro. The safe value of ADI for As in the drinking water is 0.66 µg/kg/day (Table 5, 6) [36].

Table 4. **Descriptive statistics of As in the drinking water of Talukas Ghorabari and Mirpur Sakro in adults, children and infants.**

Taluka	**N**	**Minimum**	**Maximum**	**Mean**	**Std. Deviation**
Ghorabari	25	0.00	0.05	0.01	0.01
Mirpur Sakro	30	0.01	0.08	0.03	0.02

Table 5. **Average daily intake of As (μg/kg/d) and chronic daily intake mg/kg/day of As in drinking water of Mirpur Sakro in adults, children and infants (Safe As daily intake in water 0.66 μg/day As (μg/L).**

Sample ID	As (μg/L)	ADI (μg/kg/d)	CDI (Adult)	CDI (Children)	CDI (Infants)
M-145	35	1.884615	0.001000	0.002625	0.00280
M -146	45	2.423077	0.001286	0.003375	0.00360
M -147	11	0.592308	0.000314	0.000825	0.00088
M -148	9	0.484615	0.000257	0.000675	0.00072
M -149	23	1.238462	0.000657	0.001725	0.00184
M -150	5	0.269231	0.000143	0.000375	0.00040
M -151	22	1.184615	0.000629	0.00165	0.00176
M -152	8	0.430769	0.000229	0.00060	0.00064
M -153	11	0.592308	0.000314	0.000825	0.00088
M -154	18	0.969231	0.000514	0.00135	0.00144
M -155	21	1.130769	0.000600	0.001575	0.00168
M -156	34	1.830769	0.000971	0.00255	0.00272
M -157	10	0.538462	0.000286	0.00075	0.00080
M -158	9	0.484615	0.000257	0.000675	0.00072
M -159	22	1.184615	0.000629	0.00165	0.00176
M -160	75	4.038462	0.002143	0.005625	0.00600
M -161	66	3.553846	0.001886	0.00495	0.00528
M -162	55	2.961538	0.001571	0.004125	0.00440
M -163	22	1.184615	0.000629	0.00165	0.00176
M -164	34	1.830769	0.000971	0.00255	0.00272
M -165	5	0.269231	0.000143	0.000375	0.00040
M -166	11	0.592308	0.000314	0.000825	0.00088
M -167	6	0.323077	0.000171	0.00045	0.00048
M -168	8	0.430769	0.000229	0.00060	0.00064
M -169	33	1.776923	0.000943	0.002475	0.00264
M -170	35	4.038462	0.002143	0.005625	0.00600
M -171	45	2.423077	0.001286	0.003375	0.00360
M -172	11	3.069231	0.001629	0.004275	0.00456
M -173	9	3.392308	0.001800	0.004725	0.00504
M -174	23	0.430769	0.000229	0.000600	0.00064

Table 6. **Average daily intake of As (μg/kg/d) and chronic daily intake mg/kg/day of As in drinking water of Mirpur Sakro in adults, children and infants.**

Sample ID	As (μg/L)	ADI (μg/kg/d)	CDI (Adults)	CDI (Children)	CDI (Infants)
G-120	9	0.48	0.000257	0.000675	0.00072
G-121	12	0.65	0.000343	0.000900	0.00096
G-122	11	0.59	0.000314	0.000825	0.00088
G-123	7	0.38	0.000200	0.000525	0.00056
G-124	6	0.32	0.000171	0.000450	0.00048
G-125	0	0.00	0.000000	0.000000	0.00000
G-126	4	0.22	0.000114	0.000300	0.00032
G-127	15	0.81	0.000429	0.001125	0.00120
G-128	8	0.43	0.000229	0.000600	0.00064
G-129	7	0.38	0.000200	0.000525	0.00056
G-130	9	0.48	0.000257	0.000675	0.00072
G-131	0	0.00	0.000000	0.000000	0.00000
G-132	13	0.70	0.000371	0.000975	0.00104
G-133	17	0.92	0.000486	0.001275	0.00136
G-134	8	0.43	0.000229	0.000600	0.00064
G-135	0	0.00	0.000000	0.00000	0.00000
G-136	11	0.59	0.000314	0.000825	0.00088
G-137	18	0.97	0.000514	0.001350	0.00144
G-138	14	0.75	0.000400	0.001050	0.00112
G-139	22	1.18	0.000629	0.001650	0.00176
G-140	30	1.62	0.000857	0.002250	0.00240
G-142	45	2.42	0.001286	0.003375	0.00360
G-142	22	1.18	0.000629	0.001650	0.00176
G-143	9	0.48	0.000257	0.000675	0.00072
G-144	8	0.43	0.000229	0.000600	0.00064

Arsenic in Other Parts of Pakistan

The range of As concentration of 1 – 29 µg/L was determined in the Dera Gazi Khan, Punjab [37]. The As content range of 20–500 µg/L was reported from Rahimyar Khan, Punjab [38], while As concentrations in other parts of the country were reported as; Muzffargarh (0.01−900 µg/L) [39], Lahore (0.5−59 µg/L) [37], Sheikhupura (5–76 µg/L) [40], Peshawar (5–20 µg/L) [40], Nowshera (0.01–17.58 µg/L) [38], Khairpur (0.24−315.6 µg/L) [41], Gambat (0.01–126 µg/L) [41], Nawab Shah (10–20 µg/L) [42], Tando Allahayar (0.04–300 µg/L) [43], Thatta (10–200 µg/L) [44], and Karachi (1–80 µg/L) [45, 46].

Health Risk Assessment

The technique of assessing the unfriendly health impact within a definite time is referred to as risk assessment [47]. Cancer and non – cancer health risk may be expressed by health risk occurred by any toxic metal depends upon the quantitative measurement of risk intensity. The incremental probability that any human will produce cancer during his/her life due to the exposure of contaminants is the cancer risk. There are three major pathways of direct exposure of humans to pollutants present in water such as ingestion, inhalation and dermal contact. Cd is considered an extremely toxic element and a critical water contaminant for a long time exposure. Bones, liver and kidneys are affected badly by Cd; potential cancer risk in the breast, bladder and lung is also enhanced [48]. In the present study, carcinogenic and non – carcinogenic health hazards caused by oral ingestion of drinking water containing Cd content were measured.

Non-Cancer Risk Assessment

Because of the different adverse health effects of Cd on people, the resultant non – carcinogenic and carcinogenic risk assessments were measured. In the current study, only the ingestion route was considered among three routes of exposure like dermal absorption, inhalation and ingestion. Before calculating the HQ, chronic CDI levels were calculated (Table 7). The equation (i) was used for CDI calculations and data are given in Table 3. Infants under the age of < 1 year it was calculated that CDI values were found maximum while increasing age, these values were found to decrease. In Ghora Bari and Mirpur Sakro, variations of calculated HQ values for Cd and As exposure through drinking water ingestion are given in Table 8 and 9, respectively, in three age groups.

The average HQ levels of Cd in areas of Ghora Bari were measured as adults (0.2848), children (0.75), and infants (0.8), and in Mirpur Sakro adults (0.348), children (0.915), and infants (0.976) were measured. The range of HQ values was observed as adults (0.06 - 0.57), children (0.15 - 1.5), and infants (0.16 - 1.6) were found in the groundwater of Ghora Bari; however, the groundwater of Mirpur Sakro showed the HQ ranges as; adults (0.068 - 0.64), children (0.18 - 1.68), and infants (0.192 - 1.792). Usually, if HQ is < 1 shows no or insignificant health risk. However, if HQ is > 1 shows the existence of non – carcinogenic health risk [49].

HQ for As was measured in the drinking water of Talukas Ghorabari and Mirpur Sakro three age groups were selected for the study. About 48% of water samples declared HQ values > 1 for adults in the water of Ghorabari. Since 84% of the samples showed the HQ values > 1 for both children and infants. The HQ values for Adults of the Mirpur Sakro were observed in 63.3% samples, whereas for children and infants, HQ values were found in 100% samples. The calculated range of the HQ in the samples of Ghorabari was found as adults (0 - 4.29), children (0 – 11), and infants (0 - 12.0). However, the HQ values in the groundwater of Mirpur Sakro were measured as 0.48 - 7.14 for adults, 1.25 -18.75 for children and 1.33 - 20.0 for infants.

Table 7. **Descriptive statistics of chronic daily intake in the drinking water of Talukas Ghorabari and Mirpur Sakro in adults, children and infants.**

	N	Minimum	Maximum	Mean	Std. Deviation
CDI Adults (Ghorabari)	25	0.000000	0.001286	0.0003486	0.0002826
CDI Children (Ghorabari)	25	0.000000	0.003375	0.000915	0.0007415
CDI Infants (Ghorabari)	25	0.000000	0.003600	0.000976	0.0007909
CDI Adults (Mirpur Sakro)	30	0.000143	0.002143	0.0008058	0.0006349
CDI Children (Mirpur Sakro)	30	0.000375	0.005625	0.002115	0.0016664
CDI Infants (Mirpur Sakro)	30	0.000400	0.006000	0.002256	0.0017775

Table 8. **Cd content, CDI and HQ among three age groups residing in Taluka Mirpur Sakro.**

Sample ID	WHO Limit (3 μg/L)	Adults		Children		Infants	
	Cd (μg/L)	*CDI*	*HQ*	*CDI*	*HQ*	*CDI*	*HQ*
M-145	1.2	3.42857E-05	0.068571	0.000090	0.18	0.000096	0.192
M –146	5.2	0.000148571	0.297143	0.000390	0.78	0.000416	0.832
M –147	4.2	0.000120000	0.240000	0.000315	0.63	0.000336	0.672
M –148	4.2	0.000120000	0.240000	0.000315	0.63	0.000336	0.672
M –149	11.2	0.000320000	0.640000	0.000840	1.68	0.000896	1.792
M –150	6.2	0.000177143	0.354286	0.000465	0.93	0.000496	0.992
M –151	5.2	0.000148571	0.297143	0.000390	0.78	0.000416	0.832
M –152	8.2	0.000234286	0.468571	0.000615	1.23	0.000656	1.312
M –153	9.2	0.000262857	0.525714	0.000690	1.38	0.000736	1.472
M –154	2.2	6.28571E-05	0.125714	0.000165	0.33	0.000176	0.352
M -155	1.2	3.42857E-05	0.068571	0.000090	0.18	0.000096	0.192
M -156	3.2	9.14286E-05	0.182857	0.000240	0.48	0.000256	0.512
M -157	9.2	0.000262857	0.525714	0.000690	1.38	0.000736	1.472
M -158	1.2	3.42857E-05	0.068571	0.000090	0.18	0.000096	0.192
M -159	9.2	0.000262857	0.525714	0.000690	1.38	0.000736	1.472
M -160	2.2	6.28571E-05	0.125714	0.000165	0.33	0.000176	0.352
M -161	10.2	0.000291429	0.582857	0.000765	1.53	0.000816	1.632
M -162	6.2	0.000177143	0.354286	0.000465	0.93	0.000496	0.992
M -163	6.2	0.000177143	0.354286	0.000465	0.93	0.000496	0.992
M -164	4.2	0.000120000	0.240000	0.000315	0.63	0.000336	0.672
M -165	9.2	0.000262857	0.525714	0.000690	1.38	0.000736	1.472
M -166	1.2	3.42857E-05	0.068571	0.000090	0.18	0.000096	0.192
M -167	10.2	0.000291429	0.582857	0.000765	1.53	0.000816	1.632
M -168	7.2	0.000205714	0.411429	0.000540	1.08	0.000576	1.152
M -169	5.2	0.000148571	0.297143	0.000390	0.78	0.000416	0.832
M -170	9.2	0.000262857	0.525714	0.000690	1.38	0.000736	1.472
M -171	9.2	0.000262857	0.525714	0.000690	1.38	0.000736	1.472
M -172	6.2	0.000177143	0.354286	0.000465	0.93	0.000496	0.992
M -173	5.2	0.000148571	0.297143	0.000390	0.78	0.000416	0.832
M -174	10.2	0.000291429	0.582857	0.000765	1.53	0.000816	1.632

Table 9. **HQ in drinking water of the Ghorabari and Mirpur Sakro in adults, children and infants.**

Sample ID	Taluka Ghorabari			Taluka Mirpur Sakro			
	HQ (Adult)	*HQ (Children)*	*HQ (Infants)*	*CODE NO:*	*HQ (Adult)*	*HQ (Children)*	*HQ (Infants)*
G-120	0.86	2.25	2.40	M-145	3.33	8.75	9.33
G-121	1.14	3.00	3.20	M -146	4.29	11.25	12.00
G-122	1.05	2.75	2.93	M -147	1.05	2.75	2.93
G-123	0.67	1.75	1.87	M -148	0.86	2.25	2.40
G-124	0.57	1.50	1.60	M -149	2.19	5.75	6.13
G-125	0.00	0.00	0.00	M -150	0.48	1.25	1.33
G-126	0.38	1.00	1.07	M -151	2.10	5.50	5.87
G-127	1.43	3.75	4.00	M -152	0.76	2.00	2.13
G-128	0.76	2.00	2.13	M -153	1.05	2.75	2.93
G-129	0.67	1.75	1.87	M -154	1.71	4.50	4.80
G-130	0.86	2.25	2.40	M -155	2.00	5.25	5.60
G-131	0.00	0.00	0.00	M -156	3.24	8.50	9.07
G-132	1.24	3.25	3.47	M -157	0.95	2.50	2.67
G-133	1.62	4.25	4.53	M -158	0.86	2.25	2.40
G-134	0.76	2.00	2.13	M -159	2.10	5.50	5.87
G-135	0.00	0.00	0.00	M -160	7.14	18.75	20.00
G-136	1.05	2.75	2.93	M -161	6.29	16.50	17.60
G-137	1.71	4.50	4.80	M -162	5.24	13.75	14.67
G-138	1.33	3.50	3.73	M -163	2.10	5.50	5.87
G-139	2.1	5.50	5.87	M -164	3.24	8.50	9.07
G-140	2.86	7.50	8.00	M -165	0.48	1.25	1.33
G-142	4.29	11.2	12.00	M -166	1.05	2.75	2.93
G-142	2.10	5.50	5.87	M -167	0.57	1.50	1.60
G-143	0.86	2.25	2.40	M -168	0.76	2.00	2.13
G-144	0.76	2.00	2.13	M -169	3.14	8.25	8.80
				M -170	7.14	18.75	20.00
				M -171	4.29	11.25	12.00
				M -172	5.43	14.25	15.20
				M -173	6.00	15.75	16.80
				M -174	0.76	2.00	2.13

Carcinogenic Risk Assessment

The IARC and the WHO have categorized Cd as a carcinogenic contaminant [50]. The ILCR may be used to assess the potential cancer risks because of exposure to a specified level of carcinogenic pollutant. The secure range of cancer risk as given in the literature is 1.0×10^{-6} to 1.0×10^{-4} [13]. The level of $<1.0 \times 10^{-4}$ is the carcinogenic risk for multi-element, whereas, for single element cancer risk, the safe level is believed to be 1.0×10^{-6}. The results of carcinogenic risk for humans because of Cd exposure in groundwater for three age groups in Taluka Ghorabari and Mirpur Sakro are given in Table 5. In the study area of Ghorabari carcinogenic risk of Cd for 56.48% adults, 68% children, and 68% infants, whereas in Mirpur Sakro, the cancer risk of Cd for 50% adults, 86% children, and 86% infants were above the safe limit of USEPA guideline. Results of the present study revealed that the drinking water of Mirpur Sakro has a greater cancer risk than Ghorabari. The cancer risks related to adults were lower than children and infants, the major cause of this may be the body weight (Table 10 and 11).

Table 10. **Cancer risk for the people of area under study due to Cd exposure in groundwater of coastal areas of Ghorabari and Mirpur Sakro.**

Ghorabari				Mirpur Sakro			
Sample ID	***Adult***	***Children***	***Infants***	***Sample ID***	***Adults***	***Children***	***Infants***
G-120	0.000348	0.000915	0.000976	M-145	2.09E-04	0.000549	0.000586
G-121	0.000348	0.000915	0.000976	M -146	9.06E-04	0.002379	0.002538
G-122	0.00122	0.003203	0.003416	M -147	7.32E-04	0.001922	0.00205
G-123	0.000872	0.002288	0.00244	M -148	7.32E-04	0.001922	0.00205
G-124	0.001568	0.004118	0.004392	M -149	1.95E-03	0.005124	0.005466
G-125	0.001568	0.004118	0.004392	M -150	1.08E-03	0.002837	0.003026
G-126	0.001043	0.002745	0.002928	M -151	9.06E-04	0.002379	0.002538
G-127	0.000872	0.002288	0.00244	M -152	1.43E-03	0.003752	0.004002
G-128	0.001745	0.004575	0.00488	M -153	1.60E-03	0.004209	0.00449
G-129	0.00122	0.003203	0.003416	M -154	3.83E-04	0.001007	0.001074
G-130	0.000523	0.001373	0.001464	M -155	2.09E-04	0.000549	0.000586
G-131	0.001397	0.00366	0.003904	M -156	5.58E-04	0.001464	0.001562
G-132	0.00122	0.003203	0.003416	M -157	1.60E-03	0.004209	0.00449
G-133	0.001397	0.00366	0.003904	M -158	2.09E-04	0.000549	0.000586
G-134	0.000348	0.000915	0.000976	M -159	1.60E-03	0.004209	0.00449
G-135	0.000174	0.000458	0.000488	M -160	3.83E-04	0.001007	0.001074
G-136	0.000523	0.001373	0.001464	M -161	1.78E-03	0.004667	0.004978
G-137	0.000523	0.001373	0.001464	M -162	1.08E-03	0.002837	0.003026
G-138	0.000348	0.000915	0.000976	M -163	1.08E-03	0.002837	0.003026
G-139	0.001397	0.00366	0.003904	M -164	7.32E-04	0.001922	0.00205
G-140	0.000174	0.000458	0.000488	M -165	1.60E-03	0.004209	0.00449
G-142	0.000348	0.000915	0.000976	M -166	2.09E-04	0.000549	0.000586
G-142	0.000348	0.000915	0.000976	M -167	1.78E-03	0.004667	0.004978
G-143	0.001043	0.002745	0.002928	M -168	1.25E-03	0.003294	0.003514
G-144	0.00122	0.003203	0.003416	M -169	9.06E-04	0.002379	0.002538
				M -170	1.60E-03	0.004209	0.00449
				M -171	1.60E-03	0.004209	0.00449
				M -172	1.08E-03	0.002837	0.003026
				M -173	9.06E-04	0.002379	0.002538
				M -174	1.78E-03	0.004667	0.004978

Table 11. Descriptive statistics of carcinogenic risk due to Cd among three age groups of studied area (Ghorabari and Mirpur Sakro).

Taluka Ghorabari								
Adult			**Children**			**Infants**		
Minimum	***Maximum***	***Mean***	***Minimum***	***Maximum***	***Mean***	***Minimum***	***Maximum***	***Mean***
0.00017446	0.0017446	0.000872	0.000458	0.004575	0.002288	0.000488	0.00488	0.00244
Taluka Mirpur Sakro								
Adult			**Children**			**Infants**		
Minimum	***Maximum***	***Mean***	***Minimum***	***Maximum***	***Mean***	***Minimum***	***Maximum***	***Mean***
0.000209143	0.001952	0.001063	0.000549	0.005124	0.002791	0.000586	0.005466	0.002977

Conclusion

The research was carried out for Cd and As concentration determination from 55 sampling points of Ghorabari and Mirpur Sakro in coastal area, non-carcinogenic and carcinogenic health risks were also calculated for three age groups i.e., adults, children, and infants. Important information was obtained from the current study on the poisonous effect of Cd in the drinking water of the studied area regarding health risk. The residents of the area were observed to have depressed living pattern and could not know the quality of water, therefore were interviewed regarding their health and replied to suffer from various diseases. Cd content higher than the WHO limit of 3 µg/L has been observed in 56% and 80% samples of Talukas Ghorabari and Mirpur Sakro, respectively. The value of HQ was found within a safe limit for adults, while 40% of both children and infants showed HQ value >1 from groundwater of the studied area, which may cause non-carcinogenic risk to the people of the area. The risk levels were compared and found in the order of infants > children > adults. The concentration of As was found greater than the allowable limit of 10 µg/L in 48% of samples of Taluka Ghorabari. The results reveal that 63.3% of samples showed the ADI greater than the safe limit in the drinking water of Mirpur Sakro. The HQ values in the case of As greater than one were observed in 48% water samples for adults since 84% of the samples showed the HQ values > 1 for both children and infants in Taluka Ghorabari. Regarding As HQ values> 1 were observed in 63.3% samples for adults and 100% for both children and infants. It may be noted that higher risk levels may be observed if more toxic metals are determined in the study area. Therefore, it is the responsibility of the government of Pakistan to take severe actions and involvement to provide safe drinking water either by treatment of the groundwater or finding alternate sources to decrease the health hazard of Cd and As susceptibility to the people of the area under study.

Conflicts of Interest

The authors declare that there is no conflict of interest.

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