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Monitoring of Elemental Contamination in Groundwater Samples of Sobhodero Khairpur, Sindh, Pakistan

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Abstract: The aim of present study was to monitor arsenic and other trace and toxic elemental exposure in groundwater ofT aluka Sobhodero being most populous Taluka of District Khairpur, Sindh, Pakistan. 333 groundwater samples were collected on the basis of Union Councils throughout Taluka Sobhodero. Among 333 samples, 90 were collected from tube well (90-TW) and 243 were collected from hand pump (243-HP) sources in the study area. Atomic Absorption Spectroscopy (Perkin Elmer, AAS-100) was used for analysis of elemental concentrations but in case of arsenic analysis AAS coupled with mercury hydride generator MHS-15 was used in the laboratories of Institute of Chemistry, Shah Abdul Latif University, Khairpur, Pakistan. The concentrations of arsenic, copper, iron, nickel, lead and zinc were found in range of 19.5-58µgL^{-1}, 85-260µgL^{-1}, 209-412µgL^{-1}, 01-19µgL^{-1}, 06-14µgL^{-1} and 114-420µgL^{-1}respectively in HP samples and8.6-36 µgL^{-1}, 16-90 µgL^{-1}, 45-100 µgL^{-1}, 01-09 µgL^{-1}, 03-08 µgL^{-1} and 22-111µgL^{-1} correspondingly in TW samples. The proposed maximum contamination limit (MCL) for As, Cu, Fe, Ni, Pb and Zn in drinking water was10, 2000,300,20, 100, and 3000µgL^{-1} respectively as specified by WHO. The comparative study indicated that groundwater samples collected from TW sources have shown lowest levels of As, Cu, Fe, Ni, Pb and Zn as compared to HP samples possibly due to higher depths of the motor pumps.

Keywords: Arsenic; Toxic metals, Drinking water, Atomic Absorption Spectrometry

1. Introduction

Water is an essential component for survival of life on earth. It contains important minerals for humans as well as for the organisms living on earth and aquatics. Contamination of drinking water especially with toxic elements and arsenic is a major issue from both the public health and the environmental health perspectives (Huanget al. 2016; Ung-Duck et al. 2016; Huangetal. 2015). Therefore arsenic contamination in drinking water has now become a global issue and is present all over the world (Zheng et al. 2015). Arsenic is widely distributed in nature (in air, water and soil) in the form of either metalloids or chemical compounds. It is used commercially, in pesticide, wood preservative, in the manufacture of glass, paper and semiconductors. Rank wise; it is 20th element in abundance on earth's crust, 14th in seawater and 12th in human body coming from both natural and anthropogenic sources (Rezende et al. 2013;Asadullah et al. 2011; Steven et al.2012; Vinod et al. 2012).As per toxicological studies, organic arsenic was declared to be less toxic in comparison to inorganic arsenic. In general, it was found that organic arsenicals were more rapidly excreted than inorganic forms and pentavalent arsenicals were observed to be cleared faster than trivalent ones (Wang et al. 2012; Spayd et al. 2012; Okkenhaug et al. 2012).

In drinking water, arsenic is found as inorganic and poses a great hazardous effect to human health. Clinical manifestations of arsenic poisoning begin with various forms of cancers including skin; bladder, lung, kidney, liver and prostate cancers. The cardiovascular and neurological effects were also attributed to inorganic arsenic (Chowdhury et al. 2015; Hossain et al. 2014; Eleni et al. 2013; Sinha et al. 2013; Douillet et al. 2013; Zivin et al. 2013).The

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contamination of water from arsenic and its health impact on human have already been reported from 23 regions in different parts of the world including Argentina, Mexico, Mongolia, Germany, Thailand, China, USA, Canada, Hungary, Romania and Vietnam (Flanagan et al. 2012; Ioannis and Athanasios 2006;Kamala et al. 2010; Yanget al.2015;Nguyenet al. 2012; Thiet al.2009; Stangeret al. 2005).

Pakistan is also facing serious public health disasters due to arsenic contaminated water and has acknowledged the need of apprizing drinking water quality and arsenic problem. Different areas of our country have high arsenic concentration in drinking water including ground and surface water (Muhammad Qasim and Mushtaque Ali2017; Fakir et al. 2016; Seema et al. 2016;Sardar et al. 2015; Atta et al. 2016; Sadia et al. 2015; Toqeer et al. 2015; Abbas et al. 2013; Khan et al. 2013;Jakhrani et al. 2011;Baiget al. 2010).

Therefore, the aim of our present study was to evaluate the concentration level of arsenic and other toxic elements in groundwater of Sobhodero and its surroundings with special emphasis to arsenic contamination possibly coming through drinking water sources because in the study area analysis of arsenic concentration in drinking water was not carried out so far, by any government organization or other national agency.

2. MATERIALS AND METHODS

2.1 Study Area

Sobhodero District Khairpur is lying between 27^{o} 32'-73^{o} 40 north latitudes and 68^{o} 37' 19^{o} 32'east longitudes. The study area of present research work is Sobhodero Taluka District Khairpur Mir's which is an agricultural and fertile land and is comingin region of cotton belt of the province of Sindh, Pakistan. TalukaSobhodero comprises nine Union Councils (UCs) namely, Sobhodero, Ranipur, Hingorja,Madd, Sami, Saghyoon,Pirhiyat Shah,Rasoolabad and Gadhiji. The area is covered almost with rural population settled in villages, some small cities with good populationare also available such as Ranipur, Hingorja and Sobhedero itself. The study area is located at the northern part of Sindh province of Pakistan as shown in **Figure-1**. Moreover, study area is a subtropical region, mostly cold in winter and hot in the summer. The range of temperature is 4 to 46 ^{0}C having more than 230mm average rainfall (Shrestha et al. 2002).

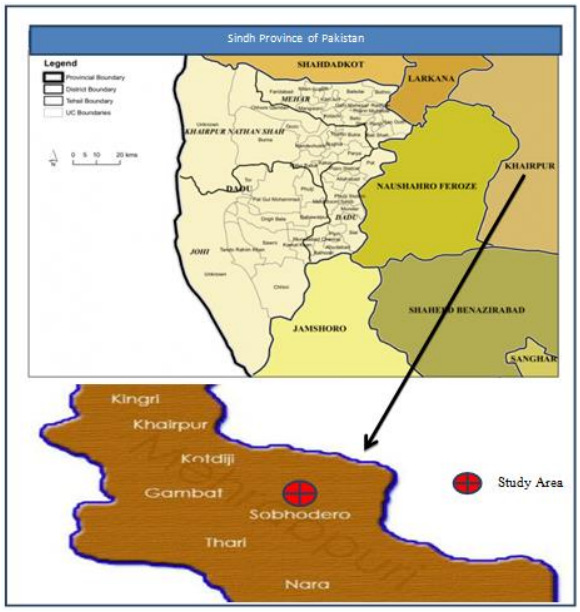

Figure 1: Map of Sindh, Pakistan, Showing study area.

2.2 Collection and Pretreatment of water Samples

Three hundred and thirty three (333) groundwater samples were collected form Sobhodero Taluka District Kahirpur on the basis of the Union Councils from various sampling points. The samples were taken in 500ml polyethylene plastic bottles. Cluster sampling protocol was adopted throughout the work. Samples were collected from tube well and hand pumps by applying below mentioned procedure. After filling water samples in 500 ml plastic (polyethylene) bottles, the bottles were marked with waterproof labels and dully coded for identification. The pre-treatment of the samples was performed as described in paper (Muhammad Qasim and Mushtaque Jakhrani 2017). The pretreated samples were then preserved by adding 10% HNO_3 to bring the pH of samples less than 2.0. For samples having neutral pH, approximately, 2.5ml of 10% HNO_3 per 0.5litter was added. The preserved samples were stored at 0-4 ^{o}C for a minimum period of 48 hours prior to analysis.

2.3 Reagents and Glassware

Double de-ionized ultrapure water was used thorough out the research work. Analytical reagent grade HNO_3 and HCl, by Merck (Darmstadt, Germany) were used. Pure Argon (99.99%) gas was used as sheath/carrier gas for atomizer. For the preparation of sodium tetra hydro borate ($NaBH_4$) solution, powdered $NaBH_4$was dissolved in 0.5M potassium iodide (KI). All the standards for analysis of As, Cu,

Fe, Ni, Pb and Zn were made by dilution method from stock standard (1000 mgL^{-1}) solutions.

2.4 Analysis of Water Samples

All tube well (TW) and hand pump (HP) water samples collected from different sites were filtered through 0.45 µm filter paper. After filtration process, the samples were placed in deep freezer at the temperature of 4°C for further analysis. Analysis in respect of Cu, Fe, Ni, Pb and Zn was carried out by using Atomic Absorption Spectroscopic technique AAS-100 Analyst by Perkin Elmer. However, As analysis was performed by using AAS coupled with Mercury Hydride Generation System (MHS15) at the Institute of Chemistry, Shah Abdul Latif University, Khairpur, Sindh, Pakistan. Temperature and pH of water samples were measured by using thermometer and portable pH meter (781-pH meter Metrohm) respectively in the field.

2.5 Statistical Analysis

Results were statistically analyzed for mean value. All results were taken in triplicate manner and reported only mean of the triplicate values. Minitab version 13 software was used along with MS XP Office 2010 version. For correlation among sampling sites and interpreted elements, Pearson correlation SPSS package was used.

3. Results and discussion

For most convenient description, groundwater samples were divided into two categories such as hand pump (HP) and tube well (TW) samples. The depth of hand pump samples (HP, $n = 243$) was varying from 35 to 40`feet and the depth of tube-well samples (TW, $n = 90$) was varying from 80 to 100 feet. The pH is one of the most important parameters to test the water quality and it is also a useful test for interpretation of water chemistry. Hence the pH of both hand pump and tube-well water samples were found neutral and it was within the WHO recommended values (6.5-8.5). The levels of As, Cu, Fe, Ni, Pb and Zn in the study area were tabulated in **Tables 1–3.**

It was found that level of arsenic was reached up to 58µgL^{-1} in Union Council Madd in sample number 122c. The obtained analysis data indicated that level of As was observed high in both HP samples and TW samples while levels of Cu, Ni and Pb in water samples were found within the safe limits as proposed by WHO. The levels of Fe and Zn were found to be slightly higher than WHO permissible limits in HP and TW samples. The results of Fe and Zn were observed in the range of 20–412µg$L^{-1}$and 15-420µgL^{-1}respectively, in HP samples, whereas09–100 µg$L^{-1}$and 01–11µgL^{-1}respectively, in TW samples. This type of work has been reported by (Muhammad Qasim and MushtaqueJakhrani2017).

Table.1.Groundwater analysis data ofdifferent Union Councils of Sobhodero, Khairpur, Sindh, Pakistan

UC-Sobhodero									*UC-Ranipur*									*UC-Hingorja*								
Sample code	pH	T (°C)	As µgL^{-1}	Cu µgL^{-1}	Fe µgL^{-1}	Ni µgL^{-1}	Pbµg L^{-1}	Zn µgL^{-1}	Samples Code	pH	T (°C)	As µgL^{-1}	Cu µgL^{-1}	Fe µgL^{-1}	Ni µgL^{-1}	Pbµg L^{-1}	Zn µgL^{-1}	Samples code	pH	T (°C)	As µgL^{-1}	Cu µgL^{-1}	Fe µgL^{-1}	Ni µgL^{-1}	Pbµ gL^{-1}	Zn µgL^{-1}
1c*	7.3	31	45.0	21	212	11	12	51	38c*	7.1	36	50.0	151	260	12	09	420	75c*	6.8	34	57.0	03	163	15	01	180
2c*	7.1	32	05.0	31	340	01	04	61	39c*	7.0	33	01.0	171	340	13	11	340	76c*	7.1	34	14.0	05	75	14	08	100
3c*	6.6	30	13.0	41	270	13	02	372	40c*	7.2	30	03.0	211	230	13	04	220	77c*	7.2	30	56.0	01	20	11	12	240
4c*	7.1	31	06.0	41	260	11	07	73	41c*	7.2	31	50.0	191	232	12	01	120	78c*	7.3	31	17.0	10	261	13	04	210
5c*	7.5	30	01.0	51	210	14	08	92	42c*	7.4	31	4.60	121	120	13	07	240	79c*	7.2	31	11.0	11	213	15	07	140
6c*	7.2	29	0.41	71	315	11	03	124	43c*	7.1	30	09.0	191	125	12	03	360	80c*	7.1	33	10.0	23	145	13	03	180
7c*	7.3	31	01.0	91	332	12	09	65	44c*	7.2	29	5.62	151	121	11	03	120	81c*	7.2	32	30.0	30	35	11	03	240
8c*	7.2	30	01.0	31	270	15	04	102	45c*	7.2	28	50.0	141	135	12	08	200	82c*	7.3	33	34.2	25	75	13	01	200
9c*	7.4	36	02.0	21	231	11	05	43	46c*	7.4	30	13.0	221	112	16	04	170	83c*	7.1	31	37.2	50	184	16	04	100
10c*	6.8	34	55.0	41	281	10	04	182	47c*	7.3	31	5.54	171	115	13	01	150	84c*	7.2	30	09.0	62	205	13	05	150
11c*	6.7	33	0.51	61	121	11	03	214	48c*	7.2	33	51.0	131	112	16	05	200	85c*	7.4	32	11.5	15	184	15	03	120
12c*	6.9	30	01.0	22	261	07	02	58	49c*	7.2	28	51.0	212	322	12	02	169	86c*	7.1	33	15.3	26	193	13	09	224
13c*	6.8	29	48.0	35	343	09	06	71	50c*	7.3	30	11.0	160	182	14	01	370	87c*	7.0	29	11.1	54	235	14	07	230
14c*	7.1	28	7.52	55	233	05	10	272	51c*	6.8	26	0.55	150	142	11	09	260	88c*	7.0	30	24.1	24	326	11	04	160
15c*	7.3	27	02.0	73	135	11	13	83	52c*	6.8	33	10.0	212	144	10	04	120	89c*	7.0	31	11.0	11	274	15	05	100
16c*	6.9	30	13.0	51	131	14	09	112	53c*	7.3	34	06.0	170	173	12	11	412	90c*	7.3	30	17.0	34	242	13	08	176
17c*	7.2	32	02.0	74	127	06	07	134	54c*	7.3	31	01.0	125	312	15	07	329	91c*	7.1	29	5.2	23	181	12	02	190
18c*	6.8	30	01.0	85	125	08	06	85	55c*	7.5	30	51.0	240	224	12	09	216	92c	6.9	29	57.0	18	206	11	07	210
19c*	7.4	32	31.0	43	134	03	05	202	56c*	7.2	30	19.0	131	152	11	03	220	93c*	7.1	31	19.0	22	182	15	03	234
20c*	7.2	31	48.0	51	116	10	09	143	57c*	7.1	32	15.0	211	274	13	04	190	94c*	7.2	32	18.8	13	143	11	02	109
21c*	7.2	30	01.0	54	114	13	07	112	58c*	7.3	33	34.0	118	244	19	02	115	95c*	7.1	31	0.42	20	75	13	09	176
22c*	6.8	33	0.81	72	113	06	06	114	59c*	7.4	30	07.0	190	253	12	09	230	96c*	7.1	30	14.0	50	65	16	11	120
23c*	7.3	30	0.55	85	212	12	05	71	60c*	6.8	29	20.0	236	260	16	02	350	97c*	6.8	28	0.43	23	211	15	04	220
24c*	6.2	31	57.0	73	140	11	08	41	61c*	6.7	31	06.0	120	340	13	05	216	98c*	6.7	29	0.41	60	183	14	07	112
25c*	6.9	34	02.0	42	170	10	05	77	62c*	6.8	31	06.0	170	230	11	08	220	99c*	7.0	32	7.40	30	203	10	11	250
26c*	7.1	32	03.0	33	166	06	07	63	63c*	6.8	34	03.0	121	133	12	04	118	100c*	7.1	33	7.71	12	182	12	12	190
27c*	7.0	30	52.0	53	101	09	03	82	64c*	6.7	34	46.0	212	132	12	07	220	101c*	7.2	36	08.0	24	112	14	09	100
28**	7.2	31	3.50	12	98	07	02	57	65c**	7.1	28	6.70	70	70	05	01	111	102c**	7.1	31	10.80	01	50	02	01	20
29**	7.2	32	2.40	8	70	04	05	54	66c**	7.5	29	12.0	90	32	02	02	70	103c**	7.2	30	3.80	03	90	09	02	13
30**	6.7	31	6.10	15	25	03	07	34	67c**	7.2	29	1.00	66	89	07	02	54	104c**	7.3	35	4.60	01	60	05	01	65
31**	7.2	33	1.00	11	40	02	03	23	68c**	7.1	30	0.90	30	50	03	03	22	105c**	7.4	34	2.10	01	30	01	02	34
32**	7.3	30	1.40	6	69	01	02	44	69c**	7.6	30	20.8	52	24	01	05	30	106c**	7.2	31	23.9	02	12	04	03	20
33**	7.4	29	1.00	11	80	02	04	41	70c**	7.1	30	4.02	69	32	09	02	20	107c**	6.9	32	25.6	03	25	02	02	12
34**	7.2	31	1.00	16	36	03	06	70	71c**	7.3	32	4.80	22	90	02	06	11	108c**	7.1	32	7.50	01	20	06	01	54
35**	7.1	30	2.0	12	24	05	03	64	72c**	7.2	32	2.81	40	16	04	03	09	109c**	7.2	31	4.80	02	14	09	03	15
36**	7.3	37	23.9	17	12	01	04	53	73c**	7.0	30	23.9	71	23	02	01	15	110c**	7.4	32	23.0	02	70	02	02	41
37**	7.1	36	0.50	11	89	02	02	33	74c**	7.1	32	3.70	23	90	08	02	08	111c**	7.2	33	3.0	01	66	01	02	12

***= hand pump groundwater samples **= tube well groundwater samples Number of analysis (n=3)**

Table.2.Groundwater analysis data of different Union Councils of Sobhodero, Khairpur, Sindh, Pakistan

UC-Madd									*UC-Sami*									*UC- Saghyoon*								
Sample code	pH	T (°C)	As µgL^{-1}	Cu µgL^{-1}	Fe µgL^{-1}	Ni µgL^{-1}	Pbµ gL^{-1}	Zn µgL^{-1}	Samples Code	pH	T (°C)	As µgL^{-1}	Cu µgL^{-1}	Fe µgL^{-1}	Ni µgL^{-1}	Pbµ gL^{-1}	Zn µgL^{-1}	Samples code	pH	T (°C)	As µgL^{-1}	Cu µgL^{-1}	Fe µgL^{-1}	Ni µgL^{-1}	Pbµ gL^{-1}	Zn µgL^{-1}
112c*	6.9	32	46.0	02	160	12	04	50	149c*	7.4	31	20.0	151	172	16	04	250	186c*	6.8	34	57.0	21	292	17	03	180
113c*	7.1	31	46.0	01	151	16	05	100	150c*	7.3	33	15.5	171	192	15	01	220	187c*	7.2	31	40.6	31	272	15	04	200
114c*	7.2	30	24.0	03	141	12	04	110	151c*	7.6	30	03.0	211	192	13	04	200	188c*	7.2	32	23.0	41	312	12	11	220
115c*	7.3	32	15.6	14	140	13	01	130	152c*	7.5	32	09.3	191	232	15	14	160	189c*	6.7	33	01.0	41	30	15	01	250
116c*	6.9	29	08.0	12	140	16	07	150	153c*	7.4	31	24.9	121	343	14	07	120	190c*	7.2	32	08.9	51	402	15	07	200
117c*	6.8	30	47.2	26	133	14	03	90	154c*	7.3	35	07.0	191	321	12	03	100	191c*	7.3	30	17.8	71	304	14	03	190
118c*	7.1	33	02.0	38	132	11	13	30	155c*	7.2	33	47.7	151	331	14	03	50	192c	7.4	29	28.0	91	335	16	03	150
119c*	6.4	33	14.5	41	128	16	03	20	156c*	7.1	34	14.3	141	292	15	05	70	193c*	7.2	33	19.0	31	316	11	12	190
120c*	6.9	31	06.0	51	124	15	04	20	157c*	7.0	32	05.6	220	352	14	04	80	194c*	7.1	30	13.7	21	384	14	04	140
121c*	7.1	33	15.8	62	121	18	05	50	158c*	7.1	29	50.3	171	312	13	05	120	195c*	7.3	32	14.9	41	304	12	05	100
122c*	7.2	30	58.0	31	132	12	04	126	159c*	7.0	30	03.0	200	333	11	03	230	196c*	7.1	34	50.2	54	312	11	04	170
123c*	7.6	32	15.0	24	128	17	11	139	160c*	7.3	31	50.3	130	362	14	05	120	197c*	6.9	34	55.3	40	412	16	06	230
124c*	7.3	29	16.7	30	124	15	12	47	161c*	7.1	33	50.4	260	405	16	13	210	198c*	6.8	31	52.1	30	341	11	03	214
125c*	7.2	28	06.0	12	123	18	10	100	162c*	7.0	32	06.1	225	352	11	06	90	199c*	7.1	28	02.0	27	272	15	09	179
126c*	7.0	29	03.0	49	117	11	03	146	163c*	7.3	30	16.6	212	391	15	08	100	200c*	7.5	29	34.1	50	263	17	04	130
127c*	7.0	27	45.0	34	116	12	04	15	164c*	7.1	28	50.0	100	352	14	14	160	201c*	7.2	28	02.4	31	210	14	03	200
128c*	7.1	28	09.0	25	114	14	05	24	165c*	7.0	29	3.12	151	255	12	09	125	202c	7.1	30	07.2	70	312	15	10	190
129c*	7.2	30	04.0	55	116	17	09	120	166c*	7.2	30	48.1	121	265	16	04	140	203c*	7.0	31	16.0	66	334	12	07	140
130c*	7.2	31	10.0	61	121	12	13	34	167c*	7.1	31	06.8	134	282	12	12	70	204c*	7.1	30	03.0	56	272	11	02	112
131c*	7.6	33	50.5	38	121	10	12	125	168c*	7.4	33	02.0	125	93	11	11	54	205c*	7.3	32	14.7	43	232	14	03	170
132c*	7.4	31	48.0	21	124	15	08	120	169c*	7.1	32	02.1	160	121	16	09	80	206c*	7.2	31	09.3	24	284	12	12	200
133c*	7.8	31	4.0	13	123	16	07	20	170c*	7.6	30	11.6	120	117	12	07	123	207c*	7.0	30	02.0	37	121	17	04	212
134c*	7.4	32	47.8	19	100	11	05	15	171c*	7.5	31	06.3	143	112	15	13	60	208c*	7.1	32	07.5	54	256	13	12	190
135c*	7.3	31	45.6	26	120	13	06	20	172c*	7.8	30	05.0	210	160	10	11	170	209c*	7.2	33	27.8	20	211	12	09	140
136c*	7.5	34	38.8	34	115	18	07	116	173c*	7.1	29	08.9	156	240	11	09	120	210c*	7.2	30	07.0	31	340	10	07	120
137c*	7.4	32	19.0	52	140	12	08	100	174c*	7.0	31	02.0	140	188	14	03	100	211c*	7.3	35	36.1	22	210	12	11	210
138c*	7.5	30	16.4	35	126	11	07	20	175c*	7.3	30	10.6	187	130	11	05	87	212c*	7.4	34	46.1	50	290	11	10	214
139c**	7.3	33	7.80	01	70	04	08	09	176c**	7.4	34	4.80	58	54	16	03	11	213c**	7.3	33	06.5	13	100	04	07	80
140c**	7.1	33	4.70	03	24	01	02	11	177c**	7.2	32	5.00	34	20	02	02	24	214c**	7.1	33	04.90	09	87	02	05	32
141c**	7.4	30	01	02	50	03	03	07	178c**	7.0	34	0.80	12	60	05	03	9	215c**	7.3	30	05.40	05	24	01	02	56
142c**	7.6	30	03	01	30	08	02	03	179c**	6.9	34	24.6	25	34	02	01	16	216c**	6.8	30	07.90	11	50	06	01	70
143c**	7.3	33	02	01	14	02	01	11	180c**	7.3	33	5.80	40	40	01	02	12	217c**	7.3	33	10.80	04	76	03	02	24
144c**	7.2	30	01	02	88	01	03	09	181c**	7.1	30	3.20	90	12	07	04	07	218c**	7.2	30	32.90	01	20	02	03	13
145c**	7.1	34	01	02	27	05	01	01	182c**	7.2	36	8.50	32	27	04	01	14	219c**	7.2	34	07.80	07	92	04	02	29
146c**	7.5	34	05	01	30	01	03	04	183c**	7.1	33	24.6	12	42	09	03	11	220c**	7.4	34	08.50	09	40	02	02	70
147c**	7.1	30	01	03	15	04	02	09	184c**	6.8	32	35.9	24	16	05	02	09	221c**	7.4	30	03.50	07	25	07	01	65
148c**	6.8	30	02	01	34	02	02	01	185c**	6.9	34	21.8	48	30	02	02	07	222c**	7.3	30	01.50	04	14	03	03	13

***= hand pump groundwater samples **= tube well groundwater samples Number of analysis (n=3)**

Table.3.Groundwater analysis data of different Union Councils of Sobhodero, Khairpur, Sindh, Pakistan

UC- PirhiyatShah									*UC- Rasoolabad*									*UC- Gadhiji*								
Sample code	pH	T (°C)	As µgL^{-1}	Cu µgL^{-1}	Fe µgL^{-1}	Ni µgL^{-1}	Pbµ gL^{-1}	Zn µgL^{-1}	Samples Code	pH	T (°C)	As µgL^{-1}	Cu µgL^{-1}	Fe µgL^{-1}	Ni µgL^{-1}	Pbµ gL^{-1}	Zn µgL^{-1}	Samples code	pH	T (°C)	As µgL^{-1}	Cu µgL^{-1}	Fe µgL^{-1}	Ni µgL^{-1}	Pbµg L^{-1}	Zn µgL^{-1}
223c*	7.2	35	19.6	151	280	03	07	20	260c*	6.7	31	10.7	191	170	14	04	40	297c*	6.9	32	49.0	81	360	11	05	20
224c*	7.1	33	13.3	171	240	04	06	20	261c*	7.2	29	15.7	121	190	02	04	40	298c*	7.1	32	10.4	101	400	02	04	50
225c*	7.4	31	50.3	41	230	02	04	20	262c*	7.1	33	09.5	41	190	03	01	50	299c*	7.2	30	6.10	61	350	03	04	40
226c*	7.3	30	15.0	91	170	05	01	20	263c*	7.2	28	28.6	41	230	05	03	50	300c*	7.3	32	12..0	51	390	04	01	40
227c*	7.3	30	10.0	121	160	01	02	40	264c*	7.3	34	13.0	51	340	08	07	60	301c*	6.9	29	19.0	31	350	08	07	50
228c*	7.2	33	01.0	41	140	06	03	40	265c*	7.1	33	11.5	141	320	09	04	70	302c*	6.8	30	6.70	11	250	05	03	40
229c*	7.2	31	19.5	41	160	09	03	50	266c*	7.2	31	8.30	221	330	08	04	60	303c*	7.1	34	49.9	11	260	06	03	30
230c*	7.1	33	50.1	51	210	09	02	60	267c*	7.3	29	5.40	171	290	07	05	40	304c*	6.4	31	9.20	11	280	12	09	30
231c*	7.3	32	11.5	71	210	12	04	20	268c*	7.1	31	4.20	131	350	02	03	40	305c*	6.9	31	10.20	21	90	07	11	80
232c*	7.4	31	3.20	91	240	02	05	20	269c*	7.2	30	11.0	151	310	05	01	70	306c*	7.1	33	9.80	31	110	09	05	30
233c*	7.1	30	50.5	134	120	10	04	34	270c*	7.4	31	7.40	50	120	11	06	35	307c*	7.2	31	48.90	30	380	11	07	50
234c*	7.1	33	48.3	121	200	04	07	40	271c*	7.1	33	11.1	100	340	13	03	54	308c*	7.6	32	7.20	70	240	09	03	30
235c*	7.2	31	47.9	111	134	08	09	30	272c*	7.0	31	7.70	120	300	04	07	60	309c*	7.3	29	7.70	101	334	07	09	22
236c*	6.9	33	3.20	121	160	03	03	25	273c*	7.0	30	23.3	140	190	06	04	40	310c*	7.2	28	6.10	11	250	02	02	30
237c*	6.9	34	56.4	32	99	06	05	40	274c*	7.0	30	26.5	23	320	02	02	65	311c*	7.0	29	8.80	54	190	08	06	34
238c*	7.2	30	09.0	100	120	09	07	60	275c*	7.3	30	58.0	40	150	03	04	70	312c*	7.0	27	6.90	76	260	11	05	49
239c*	7.1	31	14.3	123	240	05	02	54	276c*	7.1	31	28.0	121	220	06	04	54	313c*	7.1	28	11.0	40	140	04	09	45
240c*	7.6	29	19.6	112	210	13	05	34	277c*	6.9	31	15.5	171	170	08	07	70	314c*	7.2	30	31.6	34	125	02	07	20
241c*	7.1	30	03.8	190	123	02	09	45	278c*	7.1	30	16.0	120	350	03	05	40	315c*	7.2	31	8.10	100	170	12	08	50
242c*	7.0	30	57.2	50	167	11	04	30	279c*	7.2	31	01.0	70	125	09	03	34	316c*	7.6	33	51.9	50	290	09	05	25
243c*	7.2	32	57.1	112	154	13	07	60	280c*	7.1	33	20.5	41	240	05	04	60	317c*	7.4	30	23.60	45	365	07	04	54
244c*	7.3	31	40.3	70	100	10	09	25	281c*	7.1	31	21.4	90	190	02	02	45	318c*	7.8	30	15.40	34	145	12	06	23
245c*	6.9	30	16.5	39	160	06	03	40	282c*	6.8	34	03.0	50	320	12	03	30	318c*	7.4	29	42.60	25	170	09	03	60
246c*	6.8	35	08.4	54	134	08	05	34	283c*	6.7	29	7.70	120	270	01	05	66	320c*	7.3	30	4.20	40	88	04	02	25
247c*	6.7	32	09.2	100	130	04	03	20	284c*	7.0	28	50.0	118	140	03	07	50	321c*	7.5	31	15.4	89	100	02	05	40
248c*	6.9	36	14.2	120	100	05	02	50	285c*	7.1	32	6.10	56	125	09	04	70	322c*	7.4	28	7.60	35	230	05	09	60
249c*	6.8	33	22.9	65	130	10	02	25	286c*	7.2	31	7.71	70	190	05	06	40	323c*	7.5	29	18.30	70	150	03	08	30
250c**	7.4	31	23.1	20	90	03	01	09	287c**	7.2	31	0.80	20	100	01	03	21	324c**	7.1	34	10.40	13	70	01	03	14
251c**	7.3	32	03.2	12	50	01	03	02	288c**	7.1	30	4.70	13	65	03	02	16	325c**	7.4	32	07.60	17	40	04	01	11
252c**	6.7	31	20.7	09	44	02	01	07	289c**	6.8	35	16.0	22	90	02	01	09	326c**	6.8	34	12.0	9	33	02	01	11
253c**	7.2	33	03.2	14	30	02	02	11	290c**	7.4	34	05.4	17	40	05	01	11	327c**	6.7	34	15.40	11	20	01	02	05
254c**	7.3	30	12.6	18	22	03	04	02	291c**	7.2	31	09.5	20	34	01	02	13	328c**	7.2	33	06.90	05	45	03	01	09
255c**	7.1	29	24.8	21	70	04	02	08	292c**	6.9	32	03.0	09	40	04	03	07	329c**	7.1	30	04.20	08	24	03	03	12
256c**	7.2	31	02.0	08	34	02	04	05	293c**	7.1	32	08.3	13	70	02	01	02	330c**	7.6	36	08.10	03	87	02	02	11
257c**	7.1	30	26.7	05	15	01	01	13	294c**	7.3	31	11.1	07	54	03	02	09	331c**	7.1	33	07.60	08	25	03	02	07
258c**	7.3	37	03.6	11	09	03	03	09	295c**	7.1	32	07.7	23	30	02	02	02	332c**	7.0	32	10.40	02	33	01	03	04
259c**	7.1	36	01.5	02	12	03	01	06	296c**	7.1	36	01.5	05	15	01	01	04	333c**	6.9	34	06.10	08	15	03	01	02

***= hand pump groundwater samples **= tube well groundwater samples Number of analysis (n=3)**

Table.4. Statistical Percentage of Arsenic in groundwater samples of different Union Councils of Sobhodero, Khairpur, Sindh, Pakistan

Sr. No.	Sampling Sites	% of samples contaminated with As	% of samples contaminated with Cu	% of samples contaminated with Fe	% of samples contaminated with Ni	% of samples contaminated with Pb	% of samples contaminated with Zn
1.	*UC-Sobhodero*						
	Hand pump water n=27	33.3	-	3.7	-	-	3.7
	Tube well water n=10	10.0	-	-	-	-	-
2.	*UC-Ranipur*						
	Hand pump water n=27	37.0	-	14.8	-	-	25.9
	Tube well water n=10	20.0	-	-	-	-	-
3.	*UC-Hingorja*						
	Hand pump water n=27	66.6	-	3,7	-	-	-
	Tube well water n=12	40.0	-	-	-	-	-
4.	*UC-Madd*						
	Hand pump water n=27	66.6	-	-	-	-	-
	Tube well water n=10	-	-	-	-	-	-
5.	*UC-Sami*						
	Hand pump water n=27	48.1	-	40.7	-	-	-
	Tube well water n=10	40.0	-	-	-	-	-
6.	*UC-Saghyoon*						
	Hand pump water n=27	59.2	-	48.1	-	-	-
	Tube well water n=10	20.0	-	-	-	-	-
7.	*UC-Pirhiyat shah*						
	Hand pump water n=27	70.4	-	-	-	-	-
	Tube well water n=10	50.0	-	-	-	-	-
8.	*UC-Rasoolabad*						
	Hand pump water n=27	55.5	-	37	-	-	-
	Tube well water n=05	20.0	-	-	-	-	-
9.	*UC-Gadhiji*						
	Hand pump water n=27	55.5	-	29.6	-	-	-
	Tube well water n=05	40.0	-	-	-	-	-

Table-5.Temperature, pH and toxic elements ranges in groundwater samples of Sobhodero, Khairpur, Pakistan

		pH						T (^{0}C)						As					
		Hand pump			Tube well			Hand pump			Tube well			Hand pump			Tube well		
		Min	*Max*	*Mean*	*Min*	*Max*	*Mean*	*Min*	*Max*	*Mean*	*Min*	*Max*	*Mean*	*Min*	*Max*	*Mean*	*Min*	*Max*	*Mean*
	WHO	(6.5-8.5)						(25-39 ^{0}C)						10 µgL^{-1}					
1.	*UC-Sobhodero*	6.6	7.5	7.0	6.7	7.4	7.2	27	36	31	29	37	32	0.41	57.0	14.8	0.4	23.9	4.20
2.	*UC-Ranipur*	6.7	7.5	7.1	7.0	7.6	7.2	26	36	31	28	32	30	0.6	51.0	19.6	0.9	23.9	8.10
3.	*UC-Hingorja*	6.7	7.4	7.1	6.9	7.4	7.2	28	36	31	30	35	32	0.4	57.0	18.7	2.1	25.6	10.9
4.	*UC-Madd*	6.9	7.8	7.2	6.8	7.6	6.8	27	34	31	30	34	32	2.0	58.0	24.5	0.4	08.6	3.90
5.	*UC-Sami*	7.0	7.8	7.3	6.8	7.4	7.1	28	35	31	30	36	33	2.0	50.4	17.8	0.8	35.9	13.5
6.	*UC-Saghyoon*	6.7	7.5	7.2	6.8	7.3	7.2	28	35	31	30	34	32	1.0	55.3	20.5	1.5	32.9	09.0
7.	*UC-Pirhiyat shah*	6.7	7.6	7.1	6.7	7.4	6.7	29	36	32	29	37	32	1.0	57.2	24.9	1.6	26.8	12.4
8.	*UC-Rasoolabad*	6.7	7.4	7.1	6.8	7.5	7.2	28	34	31	30	35	32	1.0	58.0	15.9	0.8	16.0	7.10
9.	*UC-Gadhiji*	6.4	7.8	7.2	6.7	7.6	7.1	27	34	30	30	36	33	4.2	51.9	18.7	4.2	15.4	8.90
		Cu						Fe						Pb					
	WHO	2000 µgL^{-1}						300 µgL^{-1}						100 µgL^{-1}					
1.	*UC-Sobhodero*	21	91	52	06	17	12	101	343	202	12	98	54	02	13	06	02	07	04
2.	*UC-Ranipur*	118	240	179	22	90	53.0	112	340	201	16	90	52	01	11	05	01	06	03
3.	*UC-Hingorja*	01	62	25.0	01	03	02	20	326	169	12	90	44	01	12	06	01	03	02
4.	*UC-Madd*	01	62	30	01	03	02	100	160	127	14	88	38	01	13	07	01	08	03
5.	*UC-Sami*	100	260	166.0	12	60	34	93	405	256	12	60	33	01	14	07	01	04	02
6.	*UC-Saghyoon*	20	91	42	01	13	07	30	412	282	141	100	53	01	12	06	01	07	03
7.	*UC-Pirhiyat*	32	190	93	02	21	12	99	280	168	09	90	38	01	09	05	01	04	2.0

	shah																		
8.	*UC-Rasoolabad*	23	221	102	05	23	15	120	350	240	15	100	54	01	07	04	01	03	02
9.	*UC-Gadhiji*	11	101	49	02	17	08	88	400	240	15	87	39	01	11	06	01	03	02
		Ni						Zn											
		20 μgL^{-1}						3000 μgL^{-1}											
1.	*UC-Sobhodero*	01	15	10	01	07	03	41	372	115	23	70	47						
2.	*UC-Ranipur*	10	19	13	01	09	04	115	420	233	08	111	35						
3.	*UC-Hingorja*	10	16	13	01	09	04	100	250	173	12	65	29						
4.	*UC-Madd*	10	18	14	01	08	03	15	150	76	01	11	07						
5.	*UC-Sami*	10	16	13	01	02	05	50	250	126	07	24	12						
6.	*UC-Saghyoon*	10	17	13	01	07	03	100	250	179	13	80	45						
7.	*UC-Pirhiyat shah*	01	13	07	01	04	02	20	60	35	02	13	07						
8.	*UC-Rasoolabad*	14	14	06	01	03	02	30	70	52	02	21	09						
9.	*UC-Gadhiji*	02	12	07	01	04	02	20	80	39	02	14	09						

Table.6. Analytical ranges of data of groundwater samples of Sobhodero, Khairpur, Sindh, Pakistan

	Recommended values WHO(2010)	Hand pump n=243[a]			Tube well n=90[a]		
		Min	*Max*	*Average*	*Min*	*Max*	*Average*
pH	(6.5-8.5)	6.4	7.8	7.1	6.7	7.6	7.2
T (^{0}C)	(25-39 ^{0}C)	26	36	31	28	37	32.0
As μgL^{-1}	(0-10 μgL^{-1})	0.41	58.0	19.5	0.4	35.9	8.66
Cu μgL^{-1}	(0-2000 μgL^{-1})	70	260	85.0	01	90	16.0
Fe μgL^{-1}	(0-300 μgL^{-1})	20	412	209	09	100	45
Pb μgL^{-1}	(0-100 μgL^{-1})	01	14	06	01	08	03
Ni μgL^{-1}	(0-20 μgL^{-1})	01	19	10.6	01	09	04
Zn μgL^{-1}	(0-3000 μgL^{-1})	15	420	114	01	111	22

[a]No. of samples

Table.7. Correlation (linear) & coefficient matrix for As in HP water samples of study area.

Sr. No		UC-Sobhodero	UC-Ranipur	UC-Hingorja	UC-Madd	UC-Sami	UC-Saghyoon	UC-Pirhiyat shah	UC-Rasoolabad	UC-Gadhiji
1.	*UC-Sobhodero*	1								
2.	*UC-Ranipur*	.002	1							
3.	*UC-Hingorja*	-.036	.285	1						
4.	*UC-Madd*	.172	.094	-.233	1					
5.	*UC-Sami*	.129	.086	.186	-.287	1				
6.	*UC-Saghyoon*	.285	.348	.115	.172	.228	1			
7.	*UC-Pirhiyat shah*	-.058	.344	.084	.077	-.036	.355	1		
8.	*UC-Rasoolabad*	-.259	-.203	-.154	.022	.135	-.430*	-.238	1	
9.	*UC-Gadhiji*	.033	.392*	.210	.336	-.008	.172	.227	-.298	1

*** Correlation is significant at the 0.05 level p<0.05**

Table -8. Correlation (linear) & coefficient matrix for As in HP water samples of study area

	As	Cu	Fe	Ni	Pb	Zn
As	1					
Cu	.065	1				
Fe	.221**	.436**	1			
Ni	.186**	.268**	.360**	1		
Pb	.103	.218**	.294**	.334**	1	
Zn	.148**	.370**	.392**	.518**	.320**	1

*** Correlation is significant at the 0.05 level p<0.05 ** Correlation is significant at the 0.01level p<0.01**

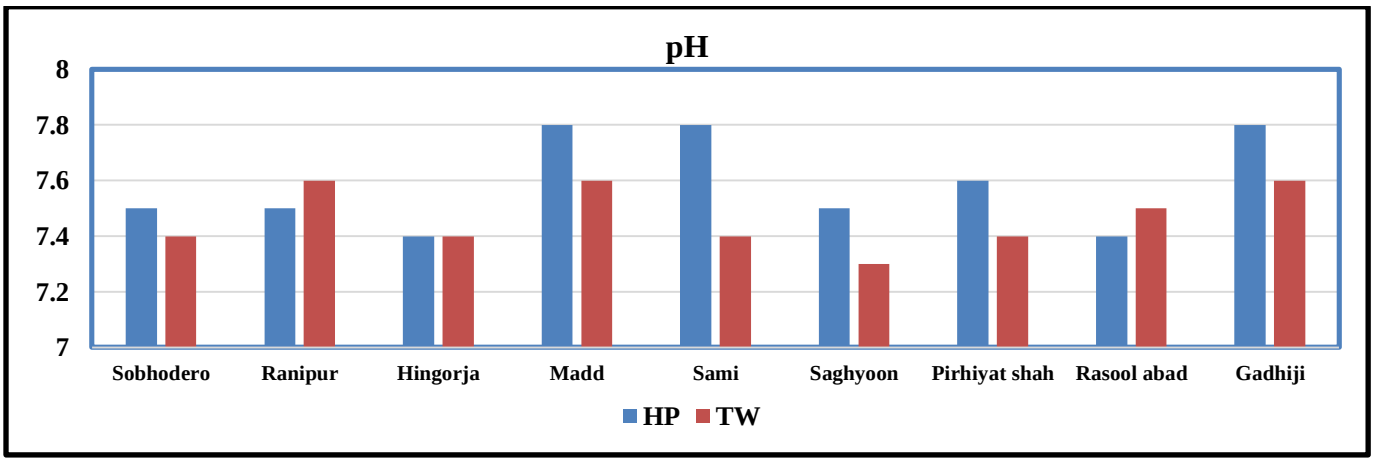

Figure 2 Comparison of pH between HP and TW samples in various Union Councils of study area.

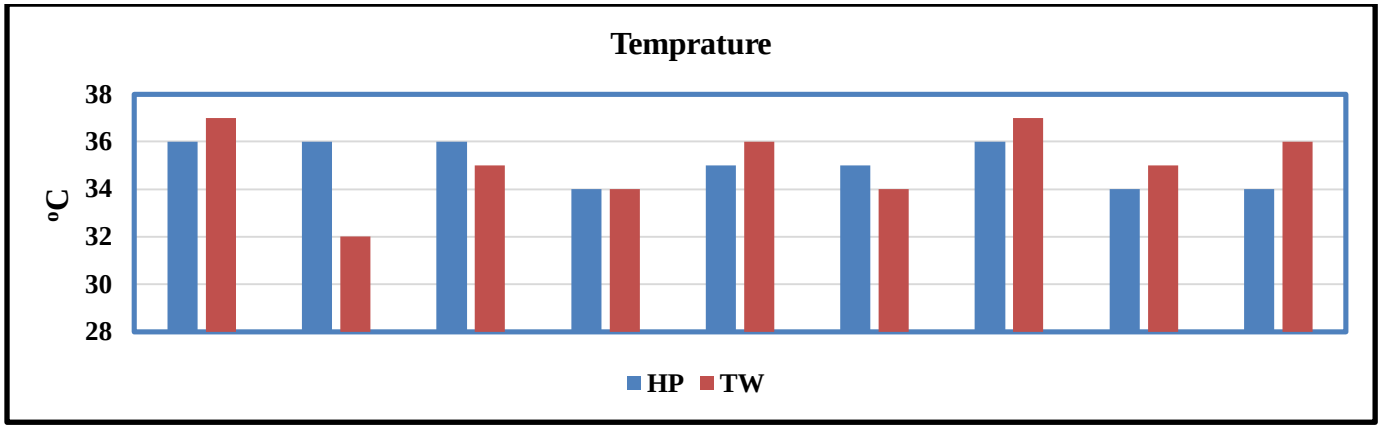

Figure 3 Comparison of temperature between HP and TW samples in various Union Councils of study area.

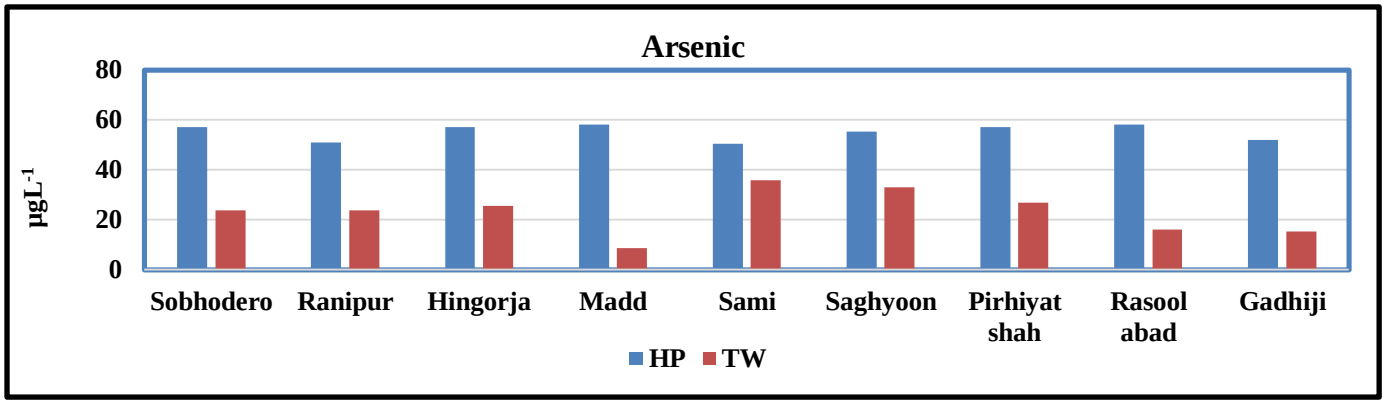

Figure 4 Comparison of arsenic concentration between HP and TW samples in various Union Councils of study area.

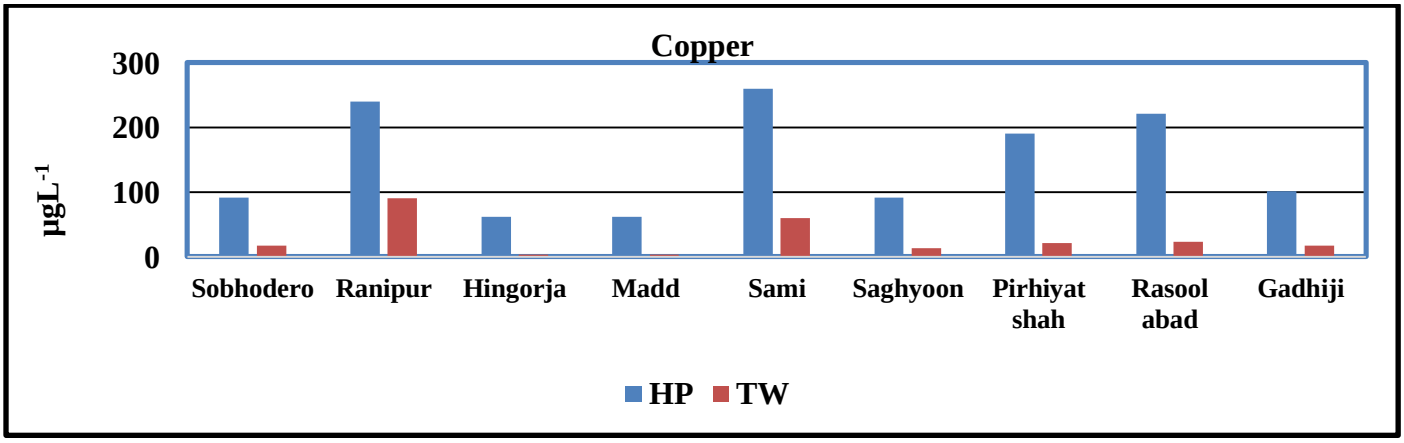

Figure 5 Comparison of copper concentration between HP and TW samples in various Union Councils of study area.

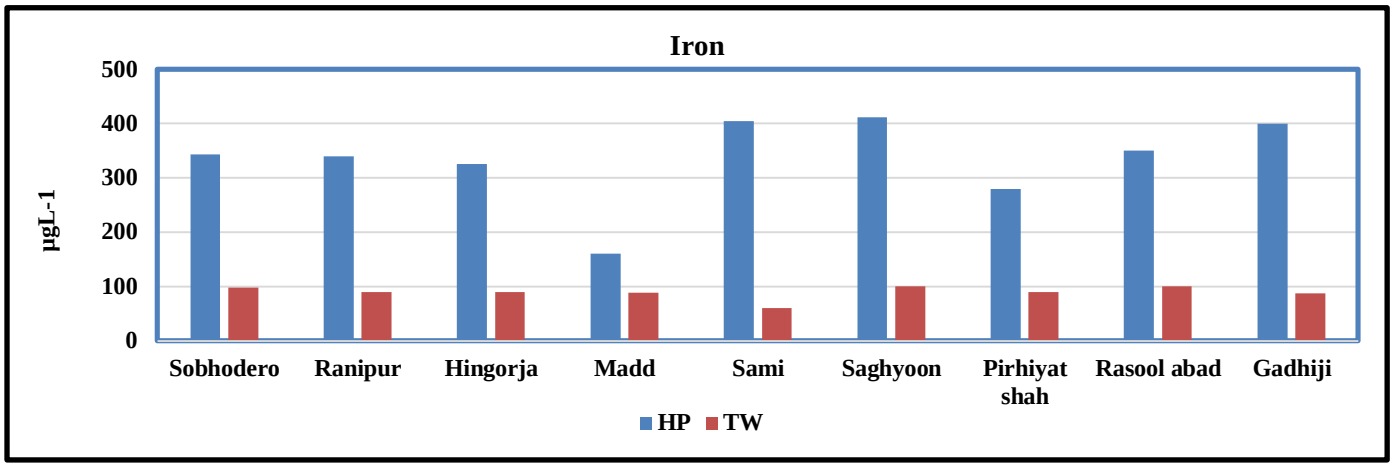

Figure 6 Comparison of iron concentration between HP and TW samples in various Union Councils of study area.

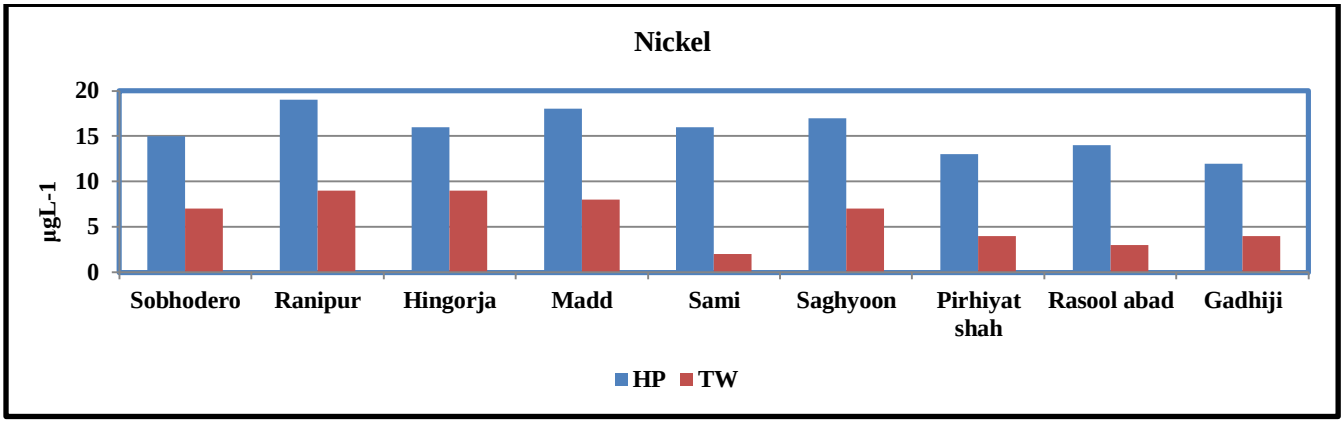

Figure 7 Comparison of nickel concentration between HP and TW samples in various Union Councils of study area.

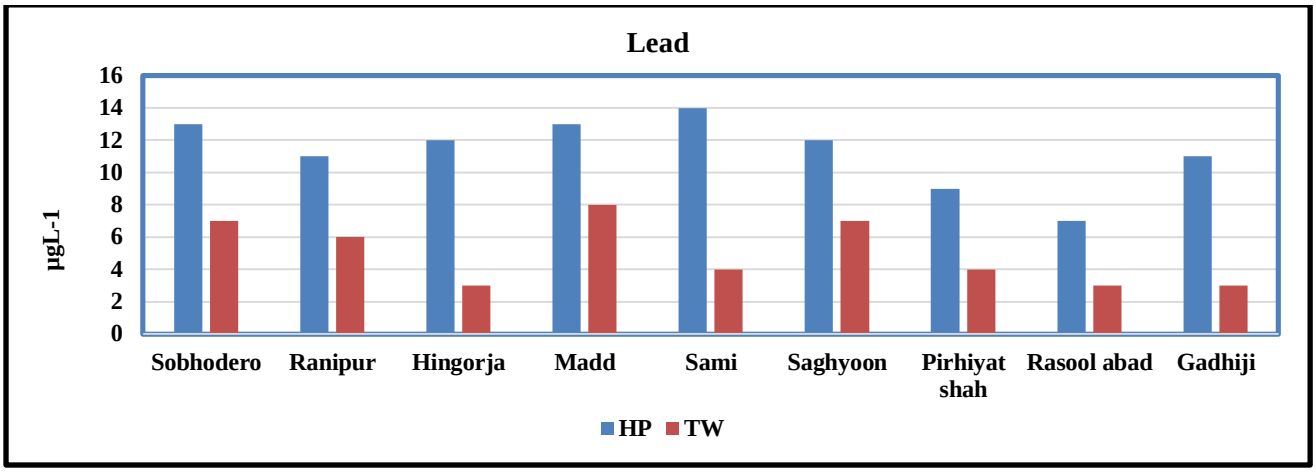

Figure 8 Comparison of lead concentration between HP and TW samples in various Union Councils of study area

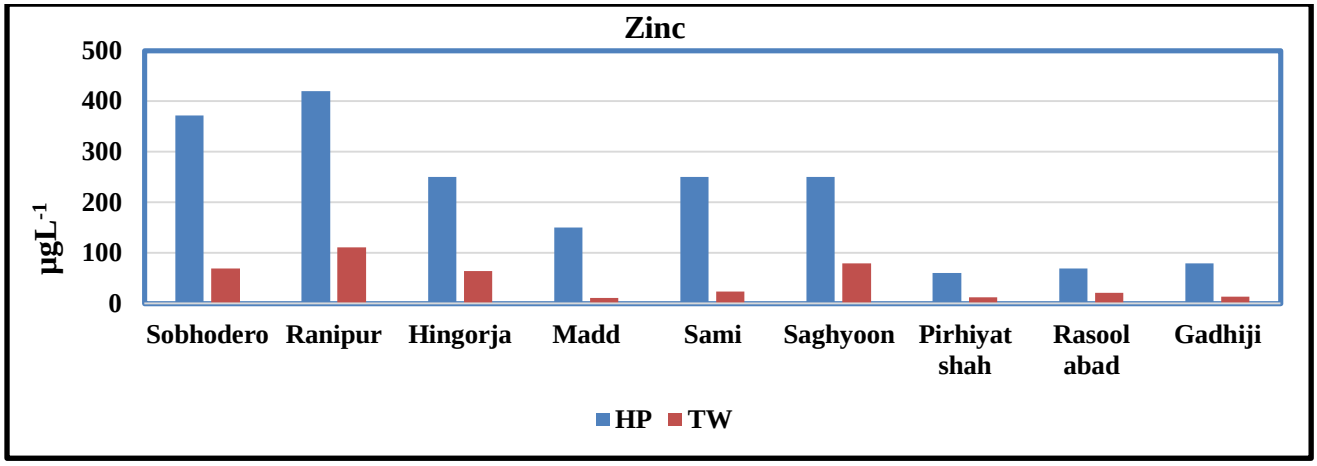

Figure 9 Comparison of zinc concentration between HP and TW samples in various Union Councils of study area.

The percentage of samples contaminated by arsenic and other elements like Cu, Fe, Ni, Pb and Zn is given in **Table-4**. In Union Council Hingorja, arsenic contamination was indicated as 66.6% in HP and 40% TW samples. Maximum number of samples examined in this Union Council showed arsenic concentration five times higher than WHO specified limit (10µgL^{-1}). The percentage of arsenic contamination at sampling site of Sobhodero, Ranipur, Hingorja, Madd, Sami, Saghyoon, pirhiyat Shah, Rasool Abad and Ghadhi was found as 33.3, 37%, 66.6%, 66.6%, 48.1%, 59.2%, 70.4%, 55.5% and 55.5% respectively, in HP samples, whereas for TW samples the respective percentages were observed as 10%, 20%, 40%, 0%, 40%, 20%, 50%, 20% and 40% correspondingly. This work is in accordance to the previously reported studies (Mandaland Suzuki 2002; Muhammad Qasim and Mushtaque Ali 2017).

Tables-5was corresponding to statistical results of all parameters of TW and HP samples in minimum and maximum values/concentrations. The levels of pH, temperature, As, Cu, Fe, Ni, Pb and Zn in ranges were found in the range of 6.4-7.8, 26-36 ^{o}C, 0.41-58µgL^{-1}, 70-260µgL^{-1}, 20-412µgL^{-1}, 0-19µgL^{-1}, 1-14µgL^{-1}and 15-420µgL^{-1}respectively in HP groundwater samples of Sobhodero, but in case TW samples the values were observed as 6.7-7.6, 28-37 ^{0}C, 0.4-36µgL^{-1}, 1-90µgL^{-1},9-100µgL^{-1}, 1-9µgL^{-1}, 1-8µgL^{-1}and 1-111µgL^{-1}correspondingly. Graphically, the comparative levels of HP and TW samples in respect to pH, temperature, As, Cu, Fe, Ni, Pb and Zn were shown in **Figures 2-7.**

The concentration of Fe was found high in HP samples while least contamination was seen in TW samples of the study area. It was observed that in Union Council Saghyoon, the maximum level of Fe was found as 412µgL^{-1} in HP sample having code number 197c* while in UC Madd, the level was observed in safe limit for Fe. The maximum Level of Fe was noted at 405µgL^{-1} in HP sample of UC Sami which was more than WHO permissible limit of (300µgL^{-1}). Samples of UC Pirhiyat were found within the safe limits while samples of UCs Gadhiji, Rasoolabad, Sobhedero, Ranipure and Hingorja were found polluted with maximum Fe concentration as 400µgL^{-1}, 350µgL^{-1}, 343µgL^{-1}, 340µgL^{-1}, 326µgL^{-1} respectively. Many studies showed that there are various ways for high level of metals in water (Hudak 2000; Finkelman et al. 2002), viz. oxidation of many arsenic ores, volcanoes and use of limitless pesticides (Welch et al. 2000). As per reports researchers, favorable conditions for the uptake of trace and toxic metals in the soil might be provided by the saline environment (Nickson et al. 2005).

The concentration of As was found almost high in HP samples as compared to TW sample in groundwater of the study area as mentioned in **Table-6.**The maximum concentration of As in HP samples was found as 58µgL^{-1}, 58µgL^{-1}, 57.2µgL^{-1}, 57µgL^{-1}, 57µgL^{-1}, 55.3µgL^{-1}, 52µgL^{-1}and 50.4µgL^{-1}whereas in TW samples maximum As concentration was found as 8.6µgL^{-1},8.6µgL^{-1}, 24.0µgL^{-1}, 26.8µgL^{-1}, 25.6µgL^{-1}, 33µgL^{-1}, 16µgL^{-1}24.0µgL^{-1}, and 36.0µgL^{-1}in UCs Madd, Rasoolabad, Pirhiyat Shah, Sobhedero, Saghyoon, Gadhiji, Ranipur and Sami respectively. In case of UC Madd, the As concentration was found within safe limit as 8.6µgL^{-1}.The observed concentration ranges of As in HP (19.5-58µgL^{-1}) and in TW (8.6-36.0µgL^{-1}) were comparatively less than other countries like Chile and Bangladesh (Sullivan 1969; Find 2001).

The enormous uses of pesticides particularly on cotton crops are responsible for soil and groundwater

contamination. Uses of fertilizer by un-educated farmer followed by non-scientific method are the major cause of groundwater pollution in the study area. Although there are many other sources of pollution of these toxic heavy metals but it has been observed that domestic waste, pesticides, fertilizer etc might be the major source of heavy metals contamination in underground and surface water (Arain et al. 2007; Wang and Shpeyzer 1997; Mandaland Suzuki 2002).

3.1 Correlation coefficient (*r*)

The correlation coefficient (*r*) indicate the extent of relationship between two variables, one estimates the presence of the other (Sidauruket al.1998*)*. The correlation coefficient among nine union councils for As in groundwater was analyzed and are given in**Table-7.**The Pearson correlation for different sampling sites indicated significant positive correlation between sampling sites Gadhiji and Ranipur(r=0.392), Saghyoon with Pirhiyat Shah (r=0.355), while negative correlation was seen between sampling site Saghyoon with Rasoolabad having regression coefficient of -.430* correspondingly.

Correlation study of As with other elements such as Cu, Fe, Ni, Pb, and Zn in HP samples of various sampling sites have been given in **Table-8.**The Table-8 indicated significant positive correlation ofNi with Zn (r= 0.518), Cu with Fe (r=0.436), Zn with Fe (r= 0. 392), Cu with Zn (r=.370), Fe with Ni (r=0.360) and Pb with Zn (r=0.320). It was observed that almost all elements showed similar magnitude of contamination in various Union Councils of Taluka Sobhodero, District Khairpur, Sindh, Pakistan.

It has been further discussed that in study area, groundwater (HP and TW water) were being used for drinking, cooking and personal hygiene. Present study shows that in many area the concentration of As and Fe is higher than the recommended safe limits of WHO. This poses a serious problem for the local Government to protect human health from As threat. There are various form of arsenic pollution in water (Baig et al. 2007). Arsenic can combine with other elements to make chemicals used to preserve wood and to kill insects on cotton and other agricultural crops. High arsenic levels may come from certain fertilizers, animal feedlots, industrial waste and herbicides (Chakrabortiet al.2002). The As poisoning status in Sobhodero, Sindh, Pakistan, is at dangerous position; so millions of people are at arsenic risk Therefore, necessary preventive measures should be adopted to minimize the risk level in the study area.

4. Conclusion

The evaluation of total arsenic, copper, iron , nickel, lead and zinc contents in hand pump groundwater (243 samples) and tube-well groundwater (90 samples) of Sobhodero, Sindh, Pakistan, were performed in order to be aware about the arsenic and other elemental pollution in the study area. It was concluded that arsenic concentration in most of HP and TW samples was higher than the WHO permissible limits. The multivariate techniques, cluster analysis of understudy sites clearly showed the high, medium and less polluted sites for hand pump and tube-well groundwater samples. Generally, in the hand pump groundwater, the level of arsenic was higher than that of tube-well water possibly due to high depth. To reduce the impact of arsenic on human health there is now a need to have particular treatment systems to remove arsenic from drinking water.

Recommendations

More detailed understanding of local sources of arsenic and mechanisms of arsenic removal is required to be evaluated. More extensive studies would be required for building practical guidance on avoiding and reducing arsenic contamination especially in groundwater of Sobhodero, Sindh, Pakistan.

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