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 of Taluka 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, 0.09-0.19µgL⁻¹, 06-14µgL⁻¹ and 114-420µgL⁻¹ respectively in HP samples and 8.6-36 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 was 10, 200, 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; Nguyen et al. 2012; Thietal. 2009; Stanger et al. 2005).

Pakistan is also facing serious public health disasters due to arsenic contaminated water and has acknowledged the need of apprising 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 Ali 2017; 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; Baig et 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° 32’-73° 40 north latitudes and 68° 37’ 19’-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. Taluka Sobhodero comprises nine Union Councils (UCs) namely, Sobhodero, Ranipur, Hingorja, Madd, Sami, Saghyoon, Pirihiyat Shah, Rasoolabad and Gadhiji. The area is covered almost with rural population settled in villages, some small cities with good population are also available such as Ranipur, Hingorja and Sobhodero 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 °C having more than 230mm average rainfall (Shrestha et al. 2002).

![Figure 1: Map of Sindh, Pakistan, Showing study area.](http://www.ijjSciences.com)

2.2 Collection and Pretreatment of water Samples

Three hundred and thirty three (333) groundwater samples were collected form Sobhodero Taluka District Khairpur 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 duly coded for identification. The pre-treatment of the samples was performed as described in paper (Muhammad Qasim and Mushtaqe Jakhrani 2017). The pretreated samples were then preserved by adding 10% HNO₃ to bring the pH of samples less than 2.0. For samples having neutral pH, approximately, 2.5ml of 10% HNO₃ per 0.5litter was added. The preserved samples were stored at 0-4 °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 HNO₃ 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 (NaBH₄) solution, powdered NaBH₄ 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 mg L\(^{-1}\)) 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 \(\mu\)m 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 58 µg L\(^{-1}\) 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 20–412 µg L\(^{-1}\) and 15–420 µg L\(^{-1}\) respectively, in HP samples, whereas 09–100 µg L\(^{-1}\) and 01–11 µg L\(^{-1}\) respectively, in TW samples. This type of work has been reported by (Muhammad Qasim and Mushtaque Jakhrani 2017).

### Table 1: Groundwater analysis data of different Union Councils of Sobhodero, Khairpur, Sindh, Pakistan

| Sample Code | pHR | T°C | AcHg | Cu | Ni | Fe | Pb | Zn | Samples Code | pHR | T°C | AcHg | Cu | Ni | Fe | Pb | Zn |
|-------------|-----|-----|------|----|----|----|----|----|------------|-----|-----|------|----|----|----|----|----|
| 1           |     |     |      |    |    |    |    |    | 2           |     |     |      |    |    |    |    |    |
| 2           |     |     |      |    |    |    |    |    | 3           |     |     |      |    |    |    |    |    |
| 3           |     |     |      |    |    |    |    |    | 4           |     |     |      |    |    |    |    |    |

* = hand pump groundwater samples  ** = tube well groundwater samples  Number of analysis (n=3)
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Table 2. Groundwater analysis data of different Union Councils of Sobhodero, Khairpur, Sindh, Pakistan

| Sample Code | T (°C) | Ca | Mg | Fe | Mn | Pb | Zn | Sample Code | T (°C) | Ca | Mg | Fe | Mn | Pb | Zn | Sample Code | T (°C) | Ca | Mg | Fe | Mn | Pb | Zn |
|-------------|--------|----|----|----|----|----|----|-------------|--------|----|----|----|----|----|----|-------------|--------|----|----|----|----|----|----|-------------|--------|----|----|----|----|----|----|-------------|--------|----|----|----|----|----|----|
| 113-1       | 18.0   | 3.0 | 4.0| 0.2| 0.2| 0.0| 0.0| 113-1       | 18.0   | 3.0 | 4.0| 0.2| 0.2| 0.0| 0.0| 113-1       | 18.0   | 3.0 | 4.0| 0.2| 0.2| 0.0| 0.0|
| 113-2       | 18.0   | 3.0 | 4.0| 0.2| 0.2| 0.0| 0.0| 113-2       | 18.0   | 3.0 | 4.0| 0.2| 0.2| 0.0| 0.0| 113-2       | 18.0   | 3.0 | 4.0| 0.2| 0.2| 0.0| 0.0|
| 113-3       | 18.0   | 3.0 | 4.0| 0.2| 0.2| 0.0| 0.0| 113-3       | 18.0   | 3.0 | 4.0| 0.2| 0.2| 0.0| 0.0| 113-3       | 18.0   | 3.0 | 4.0| 0.2| 0.2| 0.0| 0.0|

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

| Sample Code | T (°C) | Ca | Mg | Fe | Mn | Pb | Zn | Sample Code | T (°C) | Ca | Mg | Fe | Mn | Pb | Zn | Sample Code | T (°C) | Ca | Mg | Fe | Mn | Pb | Zn |
|-------------|--------|----|----|----|----|----|----|-------------|--------|----|----|----|----|----|----|-------------|--------|----|----|----|----|----|----|-------------|--------|----|----|----|----|----|----|
| 113-1       | 18.0   | 3.0 | 4.0| 0.2| 0.2| 0.0| 0.0| 113-1       | 18.0   | 3.0 | 4.0| 0.2| 0.2| 0.0| 0.0| 113-1       | 18.0   | 3.0 | 4.0| 0.2| 0.2| 0.0| 0.0|
| 113-2       | 18.0   | 3.0 | 4.0| 0.2| 0.2| 0.0| 0.0| 113-2       | 18.0   | 3.0 | 4.0| 0.2| 0.2| 0.0| 0.0| 113-2       | 18.0   | 3.0 | 4.0| 0.2| 0.2| 0.0| 0.0|
| 113-3       | 18.0   | 3.0 | 4.0| 0.2| 0.2| 0.0| 0.0| 113-3       | 18.0   | 3.0 | 4.0| 0.2| 0.2| 0.0| 0.0| 113-3       | 18.0   | 3.0 | 4.0| 0.2| 0.2| 0.0| 0.0|

* = 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         | 33.3                              | -                                | 3.7                              | -                                | -                                | 3.7                              |
|         | n=27                    |                                    |                                  |                                  |                                  |                                  |                                  |
|         | Tube well water         | 10.0                              | -                                | -                                | -                                | -                                | -                                |
|         | n=10                    |                                    |                                  |                                  |                                  |                                  |                                  |
| 2.      | UC-Ranipur              |                                   |                                  |                                  |                                  |                                  |                                  |
|         | Hand pump water         | 37.0                              | -                                | 14.8                             | -                                | -                                | 25.9                             |
|         | n=27                    |                                    |                                  |                                  |                                  |                                  |                                  |
|         | Tube well water         | 20.0                              | -                                | -                                | -                                | -                                | -                                |
|         | n=10                    |                                    |                                  |                                  |                                  |                                  |                                  |
| 3.      | UC-Hingorja             |                                   |                                  |                                  |                                  |                                  |                                  |
|         | Hand pump water         | 66.6                              | -                                | 3.7                              | -                                | -                                | -                                |
|         | n=27                    |                                    |                                  |                                  |                                  |                                  |                                  |
|         | Tube well water         | 40.0                              | -                                | -                                | -                                | -                                | -                                |
|         | n=12                    |                                    |                                  |                                  |                                  |                                  |                                  |
| 4.      | UC-Madd                 |                                   |                                  |                                  |                                  |                                  |                                  |
|         | Hand pump water         | 66.6                              | -                                | -                                | -                                | -                                | -                                |
|         | n=27                    |                                    |                                  |                                  |                                  |                                  |                                  |
|         | Tube well water         | -                                  | -                                | -                                | -                                | -                                | -                                |
|         | n=10                    |                                    |                                  |                                  |                                  |                                  |                                  |
| 5.      | UC-Sami                 |                                   |                                  |                                  |                                  |                                  |                                  |
|         | Hand pump water         | 48.1                              | -                                | 40.7                             | -                                | -                                | -                                |
|         | n=27                    |                                    |                                  |                                  |                                  |                                  |                                  |
|         | Tube well water         | 40.0                              | -                                | -                                | -                                | -                                | -                                |
|         | n=10                    |                                    |                                  |                                  |                                  |                                  |                                  |
| 6.      | UC-Sagkyoon             |                                   |                                  |                                  |                                  |                                  |                                  |
|         | Hand pump water         | 59.2                              | -                                | 48.1                             | -                                | -                                | -                                |
|         | n=27                    |                                    |                                  |                                  |                                  |                                  |                                  |
|         | Tube well water         | 20.0                              | -                                | -                                | -                                | -                                | -                                |
|         | n=10                    |                                    |                                  |                                  |                                  |                                  |                                  |
| 7.      | UC-Pirhiyat shah        |                                   |                                  |                                  |                                  |                                  |                                  |
|         | Hand pump water         | 70.4                              | -                                | -                                | -                                | -                                | -                                |
|         | n=27                    |                                    |                                  |                                  |                                  |                                  |                                  |
|         | Tube well water         | 50.0                              | -                                | -                                | -                                | -                                | -                                |
|         | n=10                    |                                    |                                  |                                  |                                  |                                  |                                  |
| 8.      | UC-Rasoolabad           |                                   |                                  |                                  |                                  |                                  |                                  |
|         | Hand pump water         | 55.5                              | -                                | 37                               | -                                | -                                | -                                |
|         | n=27                    |                                    |                                  |                                  |                                  |                                  |                                  |
|         | Tube well water         | 20.0                              | -                                | -                                | -                                | -                                | -                                |
|         | n=05                    |                                    |                                  |                                  |                                  |                                  |                                  |
| 9.      | UC-Gadhiji              |                                   |                                  |                                  |                                  |                                  |                                  |
|         | Hand pump water         | 55.5                              | -                                | 29.6                             | -                                | -                                | -                                |
|         | n=27                    |                                    |                                  |                                  |                                  |                                  |                                  |
|         | Tube well water         | 40.0                              | -                                | -                                | -                                | -                                | -                                |
|         | n=05                    |                                    |                                  |                                  |                                  |                                  |                                  |
Table 5. Temperature, pH and toxic elements ranges in groundwater samples of Sobhodero, Khairpur, Pakistan

|                  | pH     | T (°C) | As     |
|------------------|--------|--------|--------|
|                  | Hand pump | Tube well | Hand pump | Tube well | Hand pump | Tube well |
|                  | M    | M     | Me    | M    | M     | Me    | M    | M     | Me    | M    | M     | Me    | M    | M     | Me    |
| WHO              |        |        |       |       |        |       |       |       |        |       |       |        |       |        |       |
| (6.5-8.5)        |        |        |       |       | (25-39 °C) |        |       |       |        |       |        |       |       |        |
| 1. Sobhodero     |        |        |       |       |        |       |       |       |        |       |       |        |       |       |       |
| UC               | 6  | 7  | 5  | 6  | 7  | 4  | 7  | 2  | 6  | 3  | 32 | 32  | 32  | 32  | 32  | 32  |
| Ranipur          | 6  | 7  | 5  | 7  | 0  | 7  | 0  | 7  | 2  | 6  | 3  | 32 | 32  | 32  | 32  | 32  | 32  |
| Hingorja         | 6  | 7  | 4  | 6  | 9  | 4  | 6  | 2  | 6  | 3  | 32 | 32  | 32  | 32  | 32  | 32  | 32  |
| Madd             | 6  | 9  | 8  | 7  | 2  | 8  | 6  | 5  | 6  | 2  | 3  | 34  | 34  | 34  | 34  | 34  | 34  |
| Sami             | 7  | 0  | 8  | 7  | 3  | 8  | 7  | 2  | 6  | 3  | 34  | 34  | 34  | 34  | 34  | 34  | 34  |
| 6. Sahgyoon      | 6  | 7  | 5  | 7  | 2  | 8  | 7  | 3  | 7  | 2  | 34  | 34  | 34  | 34  | 34  | 34  | 34  |
| 7. Pirhiyat       | 6  | 7  | 6  | 7  | 1  | 6  | 7  | 4  | 6  | 2  | 34  | 34  | 34  | 34  | 34  | 34  | 34  |
| Shah             | 6  | 7  | 4  | 7  | 1  | 6  | 7  | 6  | 0  | 7  | 2  | 34  | 34  | 34  | 34  | 34  | 34  |
| 8. Rasoolabad     | 6  | 7  | 3  | 8  | 1  | 6  | 7  | 5  | 7  | 2  | 34  | 34  | 34  | 34  | 34  | 34  | 34  |
| 9. Gadhij           | 6  | 7  | 6  | 6  | 1  | 6  | 7  | 7  | 1  | 2  | 34  | 34  | 34  | 34  | 34  | 34  | 34  |
|                  | Cu     | Fe     | Pb     |
|                  | WHO    |        |        |        |
| Cu               |        |        |        | 2000 µg L⁻¹ |
|                  |        |        |        | 300 µg L⁻¹ |
|                  |        |        |        | 100 µg L⁻¹ |
| 1. Sobhodero     | 21 | 91 | 52 | 06 | 17 | 12 | 10 | 1 | 34 | 3 | 20 | 2 | 12 | 98 | 54 | 02 | 13 | 06 | 02 | 07 | 04 |
| 2. Ranipur       | 11 | 8  | 49 | 22 | 90 | 53  | 11 | 2 | 34 | 0 | 20 | 1 | 16 | 90 | 52 | 01 | 11 | 05 | 01 | 06 | 03 |
| 3. Hingorja      | 01 | 62 | 25  | 01 | 03 | 02 | 20 | 0 | 32 | 6 | 16 | 9 | 12 | 90 | 44 | 01 | 12 | 06 | 01 | 03 | 02 |
| 4. Madd          | 01 | 62 | 30 | 01 | 03 | 02 | 10 | 0 | 32 | 6 | 16 | 9 | 14 | 88 | 38 | 01 | 13 | 07 | 01 | 08 | 03 |
| 5. Sami          | 10 | 0  | 60 | 16 | 60 | 34 | 93 | 0 | 40 | 5 | 25 | 6 | 12 | 60 | 33 | 01 | 14 | 07 | 01 | 04 | 02 |
| 6. Sahgyoon      | 20 | 91 | 42 | 01 | 13 | 07 | 30 | 2 | 41 | 2 | 28 | 2 | 14 | 10 | 53 | 01 | 12 | 06 | 01 | 07 | 03 |
| 7. Pirhiyat       | 32 | 19 | 93 | 02 | 21 | 12 | 99 | 9 | 28 | 0 | 16 | 8 | 09 | 90 | 38 | 01 | 09 | 05 | 01 | 04 | 2.0 |
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| shah | UC-Rasool abad | UC-Gadhiji |
|------|----------------|------------|
| 8    | 23 22 1 10 2 05 23 15 12 15 0 35 0 24 0 15 10 0 54 0 1 7 0 4 0 1 0 3 0 2 | 11 10 1 49 2 02 17 08 88 40 0 24 0 15 87 39 0 1 1 0 6 0 1 0 3 0 2 |

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

|                  | Hand pump n=243* | Tube well n=90* |
|------------------|------------------|-----------------|
| **Parameter**    | **Min** | **Max** | **Average** | **Min** | **Max** | **Average** |
| pH (°C)          | (6.5-8.5) | 6.4 | 7.8 | 7.1 | 6.7 | 7.6 | 7.2 |
| T (°C)           | (25-39 °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 |

*aNo. 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    | -.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      |

* 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 0.01 level 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.
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 Gadhiji 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 (Mandalalnd Suzuki 2002; Muhammad Qasim and Mushtaque Ali 2017).

Tables 5 was 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 °C, 0.41-58µgL⁻¹, 70-260µgL⁻¹, 20-412µgL⁻¹, 0-19µgL⁻¹, 1-14µgL⁻¹and 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 °C, 0.4-36µgL⁻¹, 1-90µgL⁻¹, 9-100µgL⁻¹, 1-9µgL⁻¹, 1-8µgL⁻¹and 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, Sobheder, Ranipur 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, Sobheder, 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 at sampling site of Sobhodero, but in case 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 (Mandalalnd Suzuki 2002; Muhammad Qasim and Mushtaque Ali 2017).

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Poisoning the underwater pollution in the study area. 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 (Sidaurukel et 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), Saghyyoon with Pirhiyat Shah (r=0.355), while negative correlation was seen between sampling sites Saghyyoon 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 of Ni 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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